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XLV. *On the Relation between the Cathode Fall of Potential, the Length of the Dark Space, and the Current in the Electric Discharge through Gases.* By Sir J. J. THOMSON, O.M., F.R.S.*

Summary.

THE relation between the thickness of the dark space, the cathode fall of potential, and the current is obtained both for the normal and abnormal discharge on the suppositions that

1. The number of ions produced by an electron per cm. is proportional to $kp(V-C)/(V-C^2+M^2)$, where V is the energy of the electron expressed in volts, C the ionization potential, p the pressure, k a constant, and M the value of $V-C$ when the ionization is a maximum.
2. That the electric force in the dark space at a point P is a linear function of the distance of P from the cathode (Aston's Law).
3. That the number of electrons liberated from the cathode by the impact on it of a positive ion is $\alpha + \beta V^2$, where V is the energy of the ion. This is suggested by the experiments of Bärwald and Oliphant.

* Communicated by the Author.

4. That the relation between the potential difference V , the current density i , and the thickness of the dark space d is

$$id^2 = (\text{constant}) V^{\frac{3}{2}}.$$

On these suppositions it follows that in the abnormal discharge V varies very nearly as $(i/p^2)^{\frac{2}{3}}$ and pd as $(i/p^2)^{-\frac{1}{2}}$, where p is the pressure; thus V increases and d diminishes as the current increases.

Günther-Schulze, as the result of his experiments, gives the empirical formula V varies as $i^{\frac{1}{2}}$, so that the theory is in fair agreement with his result. The theory shows that a transverse magnetic force would diminish the thickness of the dark space, and also that it would diminish the potential difference required to produce a very short spark. The first result is well known to be true. An experiment is described which shows that the second is also true.

The result of the investigation is that the electronic collisions, though sufficient to account for the greater part of the ionization, require to be supplemented by other agents such as radiation, and an experiment is described showing the great effect on the discharge produced by radiation from the negative glow.

IN any self-sustained discharge two conditions must be satisfied; the first of these, which may be called the maintenance condition, is that there must be processes going on in the discharge which, for every electron taken from the gas by the discharge, produce another to take its place. This condition must apply whether the current passing through the gas is large or small.

The second condition is that the current density should correspond to that which the potential difference between the electrodes would send through the gas. Until the whole area of the electrodes is covered by the current, the current density may take any value within wide limits by adjustment of the area from which the current starts. Thus this condition, which is expressed as a relation between i the current density, V_0 the cathode fall of potential, and d the thickness of the dark space, will not put any limitations on the values of V_0 and d , but will determine the value of i corresponding to assigned values of these quantities. When, however, the current through the tube is so large that the discharge covers the whole of the electrode, the current density is now fixed by this current, and it is only values of

V_0 and d , which change as the current changes, which satisfy the condition. This case is often called the abnormal discharge; that when the current does not cover the electrode the normal one.

The maintenance condition will depend upon the types of ionization occurring in the discharge and the laws which they obey. There are many sources of ionization in the discharge, collisions of electrons, photoelectric effects at the cathode, and other effects due to the impact of positive ions on the cathode; the gas is also ionized by radiation excited by the discharge.

We shall begin by considering the ionization due to the collision of electrons. Experiments on the ionization produced by electrons moving with definite speeds have been made by several observers; the most recent are those by Kössel *, Hughes and Klein †, and Compton and van Voorhis ‡.

These, though they differ considerably in the numerical results, agree in their general features. The chance that an electron will produce other electrons by collisions with the molecules of the gas through which it is passing is zero until the energy of the electron reaches a definite value, which, when it is measured in volts, is called the ionization potential. After the energy passes this value the ionization is at first proportional to the difference between it and the ionization potential; it attains a maximum when the energy reaches a certain value, which, from Compton's curves, seems, for air, to be about 170 volts. Kössel gives it as 200 volts. The maximum is, however, so flat that it is very difficult to fix the exact spot at which it occurs. After the energy of the electron passes the value for maximum ionization, the ionization decreases, and is ultimately inversely proportional to the energy.

Compton's curves are in fair agreement with the formula, for which there are theoretical grounds, that the number of electrons produced per cm. of path by an electron whose energy is V , moving through a gas at pressure p , is equal to

$$\frac{kp(V - C)}{(V - C)^2 + M^2},$$

where C is the ionization potential, M the value of $V - C$ when the ionization is a maximum, and k a constant. This constant can be determined for nitrogen, since Kössel and

* Kössel, *Ann. der Phys.* xxxvii. p. 393 (1912).

† Hughes and Klein, *Phys. Rev.* xxiii. p. 450 (1924).

‡ K. T. Compton and van Voorhis, *Phys. Rev.* xxvii. p. 724 (1926).

Compton agree that in this gas the maximum ionization is such that at a pressure of 1 mm. of Hg the electron produces 10 other electrons per cm. of path.

So that, if p is measured in mm.,

$$\frac{k}{2M} = 10.$$

Taking Compton's value for M , i.e. 170 volts, $k = 3400$ for N_2 .

For hydrogen the maximum ionization at a pressure of 1 mm. is 4 electrons per cm. Compton's value of M for hydrogen is 135, hence k for hydrogen is 1080.

The number of electrons produced when the moving electron goes from $x=a$ to $x=b$ is

$$\int_a^b \frac{kp(V-C)}{(V-C)^2 + M^2} dx.$$

If the electron is starting from the cathode and moving through the cathode dark space, the value of V at a distance x from the cathode would, since Aston's experiments show that the value of the electric force is a linear function of the distance from the cathode, be given by

$$V = V_0 \frac{x(2d-x)}{d^2},$$

where V_0 is the cathode fall of potential and d the thickness of the dark space.

We shall consider this case in detail later, but it may make things clearer if we take first a hypothetical case where the analysis is simpler and suppose

$$V = V_0 \frac{x}{d},$$

which corresponds to a uniform force in the dark space.

If this is the value of V , then

$$\begin{aligned} \int_0^d \frac{kp(V-C)}{(V-C)^2 + M^2} dx &= \frac{kpd}{V_0} \int_C^{V_0} \frac{(V-C)dV}{(V-C)^2 + M^2} \\ &= \frac{kpd}{2V_0} \log \frac{(V_0-C)^2 + M^2}{M^2}. \end{aligned}$$

When V_0 is small compared with M , this is equal to

$$\begin{aligned} &\frac{kpd}{2V_0} \cdot \frac{(V_0-C)^2}{M^2} \\ &= \frac{kpd}{2} \cdot \frac{V_0-C}{M^2}, \end{aligned}$$

when C is small compared with V_0 .

When $V_0 - C$ is large compared with M , the number of electrons produced is

$$\frac{kpd}{2V_0} \log \frac{V_0^2}{M^2}.$$

The number of electrons produced is a maximum when

$$\frac{\partial}{\partial V_0} \left(\frac{1}{V_0} \log \frac{V_0^2 + M^2}{M^2} \right) = 0,$$

neglecting C in comparison with V_0 . We find that $V_0 = 2M$ is a very close approximation to the solution of this equation. For this value of V_0 the number of electrons produced by an electron travelling over the dark space is equal to

$$\frac{kpd}{4M} \log 5 = \frac{4kpd}{M}.$$

This is not very much less than $5kpd/M$, which is the number which would have been produced if the moving electron had been ionizing at the maximum rate from start to finish.

Let us now consider the case where the distribution of V is that actually found in the dark space, i.e., when

$$V = \frac{V_0}{d^2} x(2d - x)$$

or $1 - \frac{x}{d} = \sqrt{1 - \frac{V}{V_0}}$;

thus $\frac{dx}{d} = \frac{1}{2V_0} \frac{1}{\sqrt{1 - \frac{V}{V_0}}} dV$.

Hence

$$\int_0^d \frac{kpd(V - C)}{(V - C)^2 + M^2} dx = \frac{kpd}{2V_0} \int_0^{V_0} \frac{V - C}{(V - C)^2 + M^2} \cdot \frac{1}{\sqrt{1 - \frac{V}{V_0}}} dV;$$

or, putting

$$1 - \frac{V}{V_0} = y^2,$$

$$= kpd \int_0^{\sqrt{1 - \frac{C}{V_0}}} \frac{V_0(1 - y^2) - C}{(V_0(1 - y^2) - C)^2 + M^2} dy$$

$$\begin{aligned}
 &= \frac{dkp}{2} \int \left(\frac{1}{V_0(1-y^2) - C + iM} \right. \\
 &\quad \left. + \frac{1}{V_0(1-y^2) - C - iM} \right) dy \\
 &= \frac{dkp}{4V_0} \left\{ \frac{1}{\sqrt{1-\frac{C}{V_0} + \frac{iM}{V_0}}} \log \frac{\sqrt{1-\frac{C}{V_0} + \frac{iM}{V_0}} + y}{\sqrt{1-\frac{C}{V_0} + \frac{iM}{V_0}} - y} \right. \\
 &\quad \left. + \frac{1}{\sqrt{1-\frac{C}{V_0} - \frac{iM}{V_0}}} \log \frac{\sqrt{1-\frac{C}{V_0} - \frac{iM}{V_0}} + y}{\sqrt{1-\frac{C}{V_0} - \frac{iM}{V_0}} - y} \right\}.
 \end{aligned}$$

If $\frac{M}{V_0-C} = \tan \phi$ and $\alpha = \sqrt{\frac{V_0}{V_0-C}}$, this is equal to

$$\begin{aligned}
 &\frac{1}{2} \frac{dkp}{V_0} \left\{ \frac{1}{2} \sqrt{\alpha \cos \phi} \cos \frac{\phi}{2} \log \frac{y^2 + \frac{2y \cos \frac{\phi}{2}}{\sqrt{\alpha \cos \phi}} + \frac{1}{\alpha \cos \phi}}{y^2 - \frac{2y \cos \frac{\phi}{2}}{\sqrt{\alpha \cos \phi}} + \frac{1}{\alpha \cos \phi}} \right. \\
 &\quad \left. - \sqrt{\alpha \cos \phi} \sin \frac{\phi}{2} \tan^{-1} \frac{\left(2y \sin \frac{\phi}{2} \sqrt{\alpha \cos \phi} \right)}{1 - y^2 \alpha \cos \phi} \right\}. \quad (1)
 \end{aligned}$$

This represents the indefinite integral. When the electron travels through the dark space, *i.e.*, from $x=0$ to $x=d$, the limits of integration when C/V is small are $y=0$, $y=1$, and between these limits the integral in this case is equal to

$$\begin{aligned}
 &\frac{1}{2} \frac{dkp}{V_0} \left\{ \sqrt{\cos \phi} \cos \frac{\phi}{2} \log \frac{\cos \frac{\phi}{2} + \sqrt{\cos \phi}}{\sin \frac{\phi}{2}} \right. \\
 &\quad \left. - \sin \frac{\phi}{2} \sqrt{\cos \phi} \tan^{-1} \frac{\sqrt{\cos \phi}}{\sin \frac{\phi}{2}} \right\}. \quad \quad (2)
 \end{aligned}$$

From this equation the number of electrons produced by an electron starting from the cathode and travelling through

the dark space can be calculated for various potential falls V_0 . The results are shown in the following table. The number of electrons produced is expressed as a fraction of $kdp/2M$, the number which would be produced if the electron from start to finish were moving with the velocity for maximum ionization.

$\frac{V_0}{M}$5	1	1.25	1.5	1.75	2	3	4	.6
Number of electrons...		.60	.81	.85	.86	.85	.83	.73	.62	.53

This table shows that the number of electrons produced is a maximum when $V_0 = 1.5 M$. For some gases this value of V_0 seems to be not far from the truth; the values of M are, however, difficult to determine with accuracy. We see from this table that, though the velocity of the electron is changing throughout its passage through the dark space, there is a considerable range of cathode falls for which it produces more than 80 per cent. of the maximum number it is possible for an electron to produce.

It follows from the expression (2) that when V_0/M is very large, and therefore ϕ small, the number of electrons produced is equal to

$$\frac{1}{2} \frac{kpd}{V_0} \log \frac{4V_0}{M}. \quad \dots \quad (3)$$

Since the logarithm varies slowly, the number of electrons produced varies inversely as the fall of potential approximately.

The number when V_0/M is small is

$$\frac{4}{3} \cdot \frac{V_0 - C}{M} \cdot \frac{kpd}{2M}.$$

From the expression (1) we can find the number of electrons produced by the moving electron between any two points in the dark space by taking as the limits of integration the values of y corresponding to these points. If the path under consideration starts from the cathode, the upper limit of y is 1; the lower limit when the path ends where the potential is V is given by $y^2 = 1 - \frac{V}{V_0}$. By putting

$y = 1/\sqrt{2}$ we can find the number produced in the first half of the potential fall. When $V_0 = 3M/2$ the electrons produced in the first half of the potential fall are only 22 out of a total of 86 for the whole fall. Thus, in the normal discharge, about 75 per cent. of the electrons which cross the dark space have energies less than half that corresponding

to the cathode fall of potential. When, as in the abnormal discharge, the cathode fall is much greater than the normal value, the chance of an electron producing another in its passage across the dark space may be less than unity so that the majority of the electrons which cross the dark space will be those which started from the cathode, and which have the energy corresponding to the total cathode fall.

For large values of V_0 the number of electrons produced is, by equation (3),

$$\frac{kpd}{2V_0} \log \frac{4V_0}{M}.$$

pd is constant for the same gas; $kpd/2M$ is the maximum number of electrons made per centimetre of path. In nitrogen at 1 mm. pressure this number is about 10, and the dark space in nitrogen at that pressure is 3 cm., so that the number of electrons produced in the dark space is 3; hence $kpd/2M$ for nitrogen is about 3, and the number of electrons produced in the dark space

$$\frac{3M}{V_0} \log \frac{4V_0}{M}.$$

This is less than unity when V_0/M is greater than 11.5; hence, if we take the normal cathode fall as 1.5 M, the majority of the electrons leaving the dark space will have energies corresponding to the full fall of potential when the cathode fall is greater than about 8 times the cathode fall for the normal discharge.

We have hitherto considered only the electrons produced by primary electrons starting from the cathode; the secondary electrons these produce may, under the electric field in the dark space, acquire sufficient energy to ionize the gas and produce tertiary electrons, and these again may produce further electrons.

The number of electrons produced by the secondary rays can be determined by a slight modification of the preceding method. We must in equation (1) replace d by l (the length of the path of the secondary electron in the dark space), and V_0 (the cathode fall of potential) by $V_0 l^2/d^2$, which is the potential through which the secondary electron falls.

The figures we have given show that when the potential difference is of the order of that corresponding to the normal discharge, the ionization is within a few per cent. of that which an electron would produce if it were ionizing at the maximum rate over the whole of its path. Under these

circumstances the ionization by secondary and tertiary electrons would be very important, and make the ionization proportional to $e^{kpd} - 1$, rather than to kpd .

In the abnormal discharge, where the number of secondaries produced is small compared with the primaries, the subsidiary ionization would be insignificant and the ionization proportional to kpd .

The production of electrons in the gas by the collisions of electrons moving away from the cathode cannot by itself be sufficient to maintain the discharge; there must be some other process going on which will renew the supply of electrons coming from the cathode. The positive ions which are produced in the ionization by the electronic collisions will be driven on to the cathode by the electric force in the dark space. It is a well-established fact that the impact of positive ions against a metal plate causes it to emit electrons, the number emitted depending on the energy of the positive ions when they strike the plate, and increases rapidly as this energy increases. The graphs given by Bärwald (*Ann. Phys.* ix. p. 1, 1919) and Oliphant (*Proc. Camb. Phil. Soc.* xxiv. p. 451, 1928) for the relation between the number of electrons expelled from the plate by the impact of an ion and the energy of the ion, suggest that N , the number of electrons, is given by an equation of the form

$$N = \alpha + \beta V^2, \dots \quad (4)$$

where V is the potential difference through which the ion striking the plate has fallen. There are some theoretical considerations in favour of this relation, since the depths to which the ions penetrate is proportional to the square of their energy. And even if the ions have no energy when they strike against the plate, when they get neutralized by receiving an electron, they will emit radiation, and this radiation, by its photoelectric effects on the cathode, will give rise to the emission of electrons. Oliphant (*loc. cit.*) has shown that the emission of electrons by the impact of positive ions is much influenced by layers of gas on the electrode. As in experiments on discharge through gases the electrodes are always in contact with gas at not infinitesimal pressures, there will always be layers of gas on the cathode, and its behaviour may depend more on the nature of these layers than on the metal of which it is made.

Assuming then that the expression holds for the electrons ejected by a positive ion, the number of positive ions produced by an electron in its passage through the dark space is equal to the number of electrons which it produces, and

for which we have found expressions. Let $F(kpd, V_0)$ be the number of positive ions produced; the number of electrons which these will expel when they strike against the cathode will be of the form

$$F(kpd, V_0)(\alpha + \beta V^2).$$

If this number is equal to 1, then every electron which starts from the cathode and passes through the dark space will automatically provide a successor, so that the discharge will be self-sustained; hence the maintenance equation is

$$F(kpd, V_0)(\alpha + \beta V_0^2) = 1.$$

The numbers given in the table on p. 399 for the number of electrons produced by a single electron moving through the dark space can be represented with considerable accuracy by the expression

$$\frac{kpd \cdot V_0}{V_0^2 + U^2},$$

where $U = 1.5$ M. To represent the effect of the ionization due to secondary, tertiary, and higher orders of electrons, we may replace this expression by

$$\epsilon^{\frac{kpd \cdot V_0}{V_0^2 + U^2}} - 1,$$

and the maintenance equation is

$$\left(\epsilon^{\frac{kpd \cdot V_0}{V_0^2 + U^2}} - 1 \right) (\alpha + \beta V_0^2) = 1.$$

When $\frac{kpd \cdot V_0}{V_0^2 + U^2}$ is small, this becomes

$$\frac{kpd \cdot V_0}{V_0^2 + U^2} (\alpha + \beta V_0^2) = 1. \quad \dots \quad (5)$$

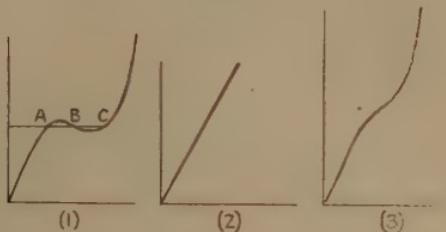
The function $\frac{V_0(\alpha + \beta V_0^2)}{V_0^2 + U^2}$ is represented by graphs of the types (1), (2), (3), fig. 1, according as α/β is greater than, equal to, or less than U^2 .

Thus, when the graph is of the type (1), there will, when kpd is within certain limits, be three values of V_0 for a given value of pd . The solutions corresponding to the points A and C, fig. 1, (1), are stable, while that corresponding to B is unstable. Thus, under certain conditions, two types of discharge with different potential falls and different current densities are possible at the same pressure and with the same length of dark space. When the graph is of type (2) or (3)

there is only one solution for any value of pd , and only one type of discharge is possible. It is not a very infrequent experience when working with discharge through gases to find the discharge changing backwards and forwards from one type to another.

We must now consider the second condition which must be fulfilled for the discharge to be possible. This is what may be called the characteristic equation, as it expresses the

Fig. 1.



relation between the current density, the potential difference, and the distance between the electrodes. When, as in the normal discharge, the current does not cover the whole of the electrode, the current density, even when the total current is given, can have any value within wide limits; the characteristic equation determines the appropriate value of the current density, and does not put any restriction on the values of pd and V_0 .

When, however, as in the abnormal discharge, the current covers the whole of the electrode, the current density, being the total current divided by the area of the electrode, is given, and we have to choose values of V_0 and pd which satisfy this equation, as well as the maintenance one.

One example of the characteristic equation is the well-known space-charge equation

$$id^2 = \left(\frac{1}{9\pi} \sqrt{\frac{2\rho}{m}} \right) V_0^{3/2}.$$

The space-charge equation is obtained on the assumption that there is no ionization between the electrodes, and so would not apply to our case. The result,

$$id^2 = \text{constant} \times V_0^{3/2},$$

is, however, not limited to the conditions postulated in the space-charge equation. It holds, for example, when there is uniform ionization throughout the dark space, a condition

which leads to Aston's Law for the distribution of electric force. It can be shown by the method of dimensions that

$$V_0^{3/2} = id^2 \sqrt{\frac{M}{e}} \times f(w),$$

where $f(w)$ represents a function of w , and

$$w = e^4 m^{-1} i^{-2} d^{-7};$$

e is the atomic charge and m the mass of an electron. Under a considerable variety of conditions $f(w)$ seems to reduce to a constant.

We shall assume, then, that

$$id^2 = CV_0^{3/2}. \quad \dots \dots \dots \quad (6)$$

It is only in the abnormal discharge that the characteristic equation affects the relation between V_0 and pd , and in that case the ionization due to a single electron is small, so that the maintenance equation takes the form

$$\frac{kpd \cdot V_0(\alpha + \beta V_0^2)}{V_0^2 + U^2} = 1.$$

The most interesting case is when V_0 is large compared with U ; then the number of electrons produced by a single electron is, see (3), equal to

$$\frac{kpd}{2V_0} \log \frac{4V_0}{M},$$

and the maintenance equation reduces to

$$kpd V_0 \log \frac{4V_0}{M} = \text{constant}.$$

Substituting the value of d in terms of V_0 from

$$id^2 = C_1 V_0^{3/2},$$

we find

$$V_0^{7/4} \log \frac{4V_0}{M} = \text{constant} \times \left(\frac{i}{p^2} \right)^{1/2} \dots \dots \quad (7)$$

Since the solution of the equation

$$x \log x = C,$$

when x is large, is approximately $x = C/\log C$, the approximate solution of (7) is

$$V_0 = \text{constant} \times \left(\frac{\left(\frac{i}{p^2} \right)}{\log \gamma i/p^2} \right)^{2/7},$$

and, corresponding to this,

$$pd = \text{constant} \times \left(\frac{i}{p^2} \right)^{-2/7} \times \{\log \gamma(i/p^2)\}^{-3/14},$$

where γ is a constant.

Thus V_0 increases and d decreases as the current increases; both these effects are well known. Günther-Schulze (*Zeit. f. Physik*, xxiii. p. 1, 1920), as the result of a long series of measurements, proposed the empirical formula

$$V_0 \text{ varies as } i^{1/4}.$$

The preceding theory indicates that V_0 varies a little less rapidly with the current than $i^{-1/35}$, the logarithm in the denominator making the variation with i a little less rapid than the power law. The theory is thus in very fair agreement with Günther-Schulze's experiments.

When kpd is exceedingly small, we see from (5) that V_0 must be large and equal to $1/\beta kpd$. Thus the potential difference required to produce a very short spark will be inversely proportional to the length of the spark.

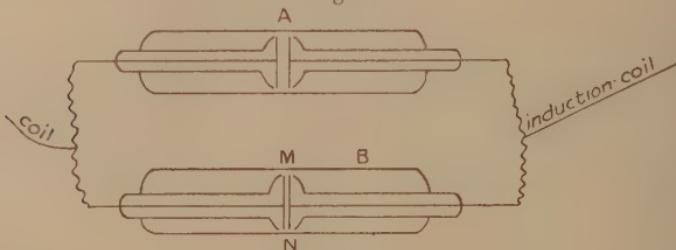
The quantity d , when it occurs in the maintenance equation, is primarily the length of path in the dark space or between the electrodes, and though this is equal to the thickness of the dark space or the distance between the electrodes when the path of the electron is along the line of electric force, it is not so when the electrons are exposed to a transverse magnetic force, which will make them describe curves whose length is greater than the distance between the electrodes. The maintenance equation gives the value of the length of the actual path, and requires this to have a definite value, whether the magnetic force acts or not. But if the curved path under the magnetic force is equal in length to the straight one when there is no magnetic force, the distance measured along the electric force, *i.e.*, normal to the electrodes, must be shorter when the magnetic force is on than when it is off; thus the thickness of the dark space must be diminished by the magnetic field. This is a well-marked and very striking phenomenon, the dark space under intense transverse magnetic fields shrinking to a fraction of its normal value.

If the distance between the electrodes is fixed, the magnetic force will increase the effective value of d , and this, by equation (5), will diminish the value of V_0 , the potential difference required to produce a spark.

I find that this effect can be shown in a very marked way in the following manner. A and B (fig. 2) are two discharge-tubes placed in parallel and connected with the terminals of

an induction-coil. The electrodes in each tube are parallel plates near together ; the distance between them in B was 1 mm., in A 2 mm. The backs of these electrodes and the wires inside the tube connecting them with the induction-coil were surrounded by glass tubes to prevent the discharge going from the backs of the electrodes. The space between the electrodes in B was between the poles M and N of a powerful electromagnet. The pressure in the tubes was adjusted within certain limits, and was such that it was far below the critical pressure for the tube B that the discharge only went through this tube with great difficulty. Then, when no current passed through the electromagnet, the discharge went entirely through A, and B was quite dark ; when, however, a current passed through the electromagnet so that there was a strong transverse magnetic field across the spark-gap in B, all the discharge went through B, and A was quite dark.

Fig. 2.



Though ionization by the collision of electrons and the ejection of electrons from the cathode by the bombardment of positive ions play a large part in maintaining the current, there are other agencies, such as the easily absorbable radiation which is produced by the discharge, which must take some part in the process. We can see by a simple calculation that it is probable that this radiation does produce an appreciable effect. We have seen that various experimenters have shown that the maximum ionization which can be produced by an electron moving through nitrogen is one electron per millimetre at a pressure of 1 mm. of Hg ; at the pressure of n millimetres n electrons would be produced per millimetre. Now, suppose that the electrons in the dark space through the whole of their path are ionizing at the maximum rate, and that the secondary electrons they produce begin as soon as they are formed to ionize at the this rate, and that this holds for all the electrons produced in the dark space ; then, when d is the thickness of the dark space, the number of electrons produced by one

electron will be e^{nd} . Now nd is constant, so that this number will not vary with the pressure. When $n=1$, the thickness of the dark space is 3 mm.; hence the number of electrons produced in the dark space is $e^3=20$. This is no doubt an overestimate, but the calculations we have given show that it is not so extravagant as might have been expected at first sight.

Along with these 20 electrons, 20 positive ions will be produced, and these will be driven against the cathode by the electric force in the dark space; thus, if the discharge is to be maintained, these 20 ions, when driven against the cathode, must liberate one electron. Thus the stream of electrons emerging from the cathode must be about 5 per cent. of the stream of positive ions impinging upon it.

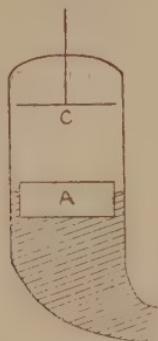
The experiments of Oliphant and Bärwald (*loc. cit.*) show that when the energy of the positive ions is of the order of that due to a fall of potential of the order of the normal cathode fall, the number of electrons ejected from a metal plate by the impact of the ions is only about 1 per cent. of the number of ions striking the plate. In the case of the dark space there is a considerable electric force at the cathode in the direction tending to remove the ions from the plate. The presence of such a field increases the emission of electrons in the ordinary photoelectric effect unless the pressure of the gas is exceedingly low, much lower than is usual when the discharge is normal. This force would have to increase the emission about five-fold to bring it up to the amount required to maintain the discharge. The numbers given seem to indicate that the electronic collisions may account for the greater part, but not for the whole, of the effect.

Another source of ionization we must consider is radiation emitted by the discharge itself. It is well known that the negative glow is especially active in emitting this radiation, so that if the help of this is required the presence of negative glow will be necessary for the discharge. To test this I tried the following experiment.

The discharge-tube (fig. 3) was cylindrical; the cathode C was a nickel disk nearly filling the cross-section of the tube; the anode A was a steel plate of the same diameter floating on the top of a column of mercury. The distance between the anode and cathode could be changed very gradually by moving the reservoir of mercury connected with the column. The discharge between A and C was produced by a battery of storage cells, and the current measured by a sensitive galvanometer. Starting from the position when A was sufficiently remote from C to allow of the development of both

the dark space and the negative glow, and making A gradually approach C, no appreciable change occurred in the current until the thickness of the negative glow was reduced to about a millimetre : then the current diminished rapidly when the approach of A to C reduced the thickness of the glow. The appearance of the discharge changed altogether, and the current was reduced to a small percentage of its original value when the thickness of the glow fell to about one-third of a millimetre ; the abruptness with which the current stopped was very striking. The presence of at least a thin piece of the negative glow appears to be essential

Fig. 3.



for the discharge. The fact that after the thickness of the dark space exceeds a millimetre or so the current is independent of the thickness is what we should expect if the glow rapidly absorbed the radiation it emits. A view that requires consideration is that the effect of the negative glow, a place where the density both of positive ions and electrons is very great, might be due not to radiation, but to the diffusion of positive ions from it into the dark space. These would be driven against the cathode by the electric field in the dark space, and there liberate electrons.

The calculation we have given above shows that if this were the explanation the number diffusing into the dark space from the negative glow would have to exceed the number of positive ions produced in the dark space itself, so that the majority of the positive ions reaching the cathode would have fallen through the whole of the cathode fall of potential, and would therefore have the maximum energy possible. The parabolas obtained in positive-ray photographs give an indication of the distribution of energy among the positive ions reaching the cathode. If the majority had the maximum energy these parabolas would have a bright

head and a faint tail. In most cases, however, the parabolas are of fairly uniform intensity, indicating that positive ions are produced pretty uniformly through the dark space.

The number of ions produced in the dark space by collisions diminishes rapidly as the cathode potential fall increases, while that due to radiation from the negative might be expected to be fairly constant, so that the radiation would be a more important factor in the abnormal discharge with large cathode falls of potential than in the normal discharge. In addition to the ionization it produces in the dark space, the radiation, when it strikes against the cathode, will, by the photoelectric effect, produce emission of electrons.

XLVI. *The Calibration of an Orifice.* By H. W. SWIFT,
*M.A., D.Sc.**

IN two earlier papers the author has attempted to place upon a rational basis certain of the more important factors which produce systematic changes in the coefficient of discharge from an orifice. This work had for its ultimate object to determine how far the marked differences in published experimental results could be explained and systematised, and to what extent the orifice could be established as a reliable and consistent, as well as sensitive, meter for fluid discharge under varying conditions. In the present paper it is proposed to consider certain other of the factors which determine the coefficient of discharge, to apply the theories put forward in an examination of the discrepancies in earlier published results, and, in the light of these considerations, to suggest methods for the calibration of an orifice in order to ensure a satisfactory registration under the various conditions of service.

The volumetric rate of flow through an orifice is commonly expressed in the form $Q = C_d \cdot a_0 \sqrt{2gH}$, where a_0 is the area of the orifice and C_d the coefficient of discharge. When conditions are such that the fluid in approach is sensibly at rest except in the immediate neighbourhood of the orifice, this expression is satisfactory, but in the more general case, when the velocity of approach is considerable, it seems better to adopt as a basis of comparison the flow

* Communicated by the Author.

of a "perfect" fluid (inviscid and incompressible) through an orifice mounted with similar conditions of approach to that under consideration and of the same size, but shaped so as to give no contraction of the jet. The quantity with which comparison is made is then $a\sqrt{2gH}$, where

$$a = \frac{Aa_0}{\sqrt{A^2 - a_0^2}},$$

A being the area of the approach chamber, a_0 that of the orifice, and H the head of the fluid. Incidentally this generalized definition, which of course reduces to the common form when approach is unrestricted, accords with that accepted for the venturimeter, and has a certain empirical justification which will appear later. In general, therefore, we shall write

$$Q = C_d \cdot a \sqrt{2gH} = C_d \cdot a \sqrt{\frac{2 \cdot \Delta p}{\rho}},$$

where ρ is the density of the fluid approaching the orifice.

The coefficient of discharge is itself regarded as the product of the coefficient of velocity C_v , the coefficient of contraction C_c , and, in the case of compressible fluids, the attenuation factor C_a . The coefficients of velocity and contraction are well-established terms; the attenuation factor is introduced to allow for the fact that the volume of a compressible fluid, when measured at its initial density, is less than that of an incompressible liquid, owing to attenuation at reduced pressures.

The effect of the various factors controlling the value of the coefficient of discharge in the case of liquid flow has been considered in some detail in the papers referred to, and the mutual reactions of the coefficients of velocity and contraction are there discussed. Under the conditions of gaseous flow these factors will in most cases operate in a similar way, but there is an additional effect which must be taken into account—the effect of compressibility.

Compressibility.

The criterion which represents the effects of compressibility in orifice flow may most simply be written $\chi = \frac{r}{\gamma}$, where

r =ratio of pressure difference to initial pressure;
 γ =ratio of specific heats.

In the case of a rounded orifice, or nozzle, the effect of compressibility is simple. Owing to the adiabatic expansion of the fluid during its passage through the orifice, the actual weight discharged is less than that calculated on the basis of the initial density, and may be determined * from this calculated quantity by the use of the "attenuation factor"

$$C_a = \frac{1}{r} \cdot \frac{\gamma}{\gamma-1} \cdot R^{2/\gamma} \left(1 - R^{\frac{\gamma-1}{\gamma}} \right) \cdot \frac{n^2 - 1}{n - R^{2/\gamma}},$$

where $R = \frac{p_2}{p_1} = 1 - r,$

$$n = \frac{A}{a_0}.$$

When, as is commonly the case in the metering of steam and gases, the ratio r is small ($r=0.1$ for atmospheric air corresponds to a water-gauge of over 40 inches), this factor, which for an inviscid fluid is the same as the coefficient of discharge, reduces to

$$C_a = \left(1 - \frac{3r}{4\gamma} \right) \sqrt{\frac{n^2 - 1}{n^2 - R^{2\gamma}}},$$

and when the orifice is small compared with the approach chamber or pipe,

$$C_a = 1 - \frac{3r}{4\gamma} \text{ nearly.}$$

In the flow through an orifice where contraction of the jet occurs there will be introduced a secondary effect of elasticity—a reaction upon the area of the contracted jet. Comparing the conditions of efflux with those of an incompressible fluid, there will be a tendency, owing to the greater density of the fluid at the orifice section compared with that at the vena contracta, for the acceleration of the fluid to be less rapid when first passing the plane of the orifice and more rapid on approaching the vena contracta. Hence the curvature of this more slowly-moving fluid under the existing pressure across the streamlines will become sharper, and a larger jet will result.

As in the case of viscosity, therefore, we have in general two contrary effects of elasticity—a reduction in discharge due to attenuation, and an increase of the area of the

* Based on St. Venant's formula (*Comptes Rendus*, 1839).

contracted jet. As a rule, in practice, these effects will both be small, and can be treated by a simple approximation.

Since orifices for the measurement of gaseous flow are commonly mounted in a pipe or duct, it will be well to use the generalized definition of the coefficient of discharge:

$$Q = C_d \cdot a \sqrt{\frac{2 \Delta p}{\rho}}, \quad \text{where } a = \frac{Aa_0}{\sqrt{A^2 - a_0^2}}.$$

If we neglect the effects of viscosity, we may also write

$$Q = C_d \cdot a' \sqrt{\frac{2 \Delta p}{\rho}}, \quad \text{where } a' = \frac{Aa_c}{\sqrt{A^2 - a_c^2}}.$$

$$\text{Hence } C_d = C_c \cdot \frac{a'}{a} = \left(1 - \frac{3r}{4\gamma}\right) \sqrt{\frac{n^2 - 1}{n_c^2 - R^{2/\gamma}}} \text{ nearly,}$$

$$\text{where } n_c = \frac{A}{a_c}.$$

When $R=1$, compressibility has no effect, so that the theoretical coefficient $C = \frac{n^2 - 1}{n_1^2 - 1}$, n_1 being the value of n_c

under ideal conditions, i. e., when discharging an inviscid liquid. Hence, when r is small, the coefficient of discharge for an elastic fluid is given by

$$\frac{C_d}{C_0} = \left(1 - \frac{3r}{4\gamma}\right) \sqrt{\frac{n_1^2 - 1}{n_c^2 - R^{2/\gamma}}},$$

and, when n is large,

$$\frac{C_d}{C_0} = \left(1 - \frac{3r}{4\gamma}\right) \frac{a_c}{a_1},$$

where a_1 corresponds to n_1 .

From a series of experiments the value of C_0 and the relation of C_d to r can be found, and the relation between a_c and a_1 deduced. The most complete and satisfactory experiments on gaseous discharge have been made by Hodgson*. Accepting his results for the discharge of air through a sharp-edged orifice, we find that,

when $n=5.6$,

$$\frac{a_c}{a_1} = 1 + 0.41r \text{ up to a value of } r=0.4,$$

and, when $n=1.4$,

$$\frac{a_c}{a_1} = 1 + 0.42r \text{ over the same range.}$$

* Inst. C. E., Sel. Paper No. 31 (1925).

Hence, when viscosity is neglected, we are in a position to express the coefficient in the form

$$C_a = C_0 \left(1 + 0.585 \frac{r}{\gamma} \right)$$

$$C_d = C_a \cdot C_c = C_0 \left(1 - \frac{1}{6} \frac{r}{\gamma} \right) \text{ very nearly.}$$

This factor may be applied with confidence to sharp orifices for values of r less than 0.2 and of n greater than 2, which covers generally the range of practical metering.

Returning now to a consideration of the joint effects of the various modifying factors, we find that for general purposes these are four in number, and may be denoted by the dimensionless criteria ξ for capillarity, η for viscosity, τ for turbulence, and χ for compressibility. The number of these factors in itself tends to complicate the problem of predicting the coefficient of discharge under assumed conditions, and this complication is further increased by the fact that they have each an effect upon, and are each affected by, the coefficient of contraction, and are therefore, to some extent, mutually reactive. Fortunately, however, the effect of each of these factors in ordinary metering practice is usually small; they are never all operative at the same time, and in those comparatively rare cases where one (either viscosity or elasticity) is important the rest, as a rule, are quite negligible.

When the effects are small, the size of the contracted jet is altered so slightly by each that the corrections due to the various component factors may be treated separately, and superposed with safety. Under such conditions a fairly simple expression can be found to cover changes in the coefficient :

$$C_d = C_0 - \kappa_1 \xi + \kappa_2 \eta + \kappa_3 \tau - \kappa_4 \chi,$$

where C_0 is the theoretical coefficient of discharge for an inviscid liquid, and ξ, η, τ, χ are the dimensionless criteria incorporating the effects of capillarity, viscosity, turbulence, and elasticity. $\kappa_1, \kappa_2, \kappa_3, \kappa_4$ are dimensionless constants sensibly independent of these criteria, but not independent of the value of C_0 .

This simple form of expression has been based on a rational treatment of the conditions of flow, and confirmed, as far as possible, by experimental tests with circular orifices. For orifices of other shapes there are no tests

available from which the effect of factors other than viscosity can be checked; but since the controlling conditions are similar, and since the results of Bovey* and Hamilton Smith† may be shown to confirm for rectangular orifices of various proportions the linear increase of the coefficient with the viscosity criterion, it is reasonable to expect that the other results are similarly applicable in a descriptive way, with a reservation in the not important case of surface tension.

A consideration of the expression from the practical point of view shows that the terms are by no means of equal importance. The corrections for capillarity and for compressibility, when these are effective, are for practical purposes quite small, and, for circular orifices at least, may be computed with sufficient accuracy without special calibration. Turbulence introduces an element of inconstancy into the flow, and it is therefore necessary, for reliable registration, to take precautions to reduce its effects to a minimum. Where this cannot be done, the consistency will necessarily suffer. It would therefore seem that in the calibration of an orifice attention is mainly centred on the basic value of the coefficient C_0 and on the viscosity term $\kappa_2 \eta$, which is always operative, and in liquid flow generally predominant.

It is now important to consider the theoretical value C_0 of the coefficient. This will depend upon two distinct circumstances—the form of orifice and the geometry of approach.

Form of Orifice.

Assuming unrestricted approach to an orifice in a plane wall as the standard condition, the value of C_0 is likely to be affected by the shape of the orifice both in and normal to this plane. There is no *a priori* reason why the coefficient should be the same for rectangular and circular orifices for example, and it is well known that a rounded orifice has a coefficient which may approach unity.

a. Effect of Rounding.

The theoretical treatment ‡ of the sharp slit orifice with

* 'Hydraulics,' p. 24.

† 'Hydraulics,' Chaps. III., XI.

‡ Kirchhoff, Crelle, lxx. (1869).

unrestricted approach shows that the free streamline is determined by the equations

$$x = 1 - \cos \theta \dots \dots \dots \dots \quad (i.)$$

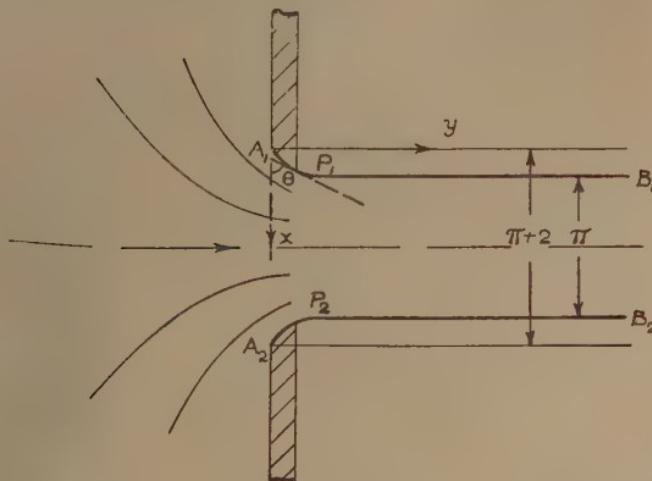
$$y = \sin \theta - \log \tan \left(\frac{\pi}{4} + \frac{\theta}{2} \right), \quad \dots \dots \quad (ii.)$$

when axes are taken as in fig. 1, and gives a value

$$\frac{\pi}{\pi+2} = 0.611$$

for the coefficient of contraction. The development of

Fig. 1.



the theory leading to these results is such as to allow an identical configuration of efflux if the sharp orifice of width $\pi+2$ be fitted with a mouthpiece conforming to and following the surface of the escaping jet to any extent whatever. Hence the known equations of the free streamlines afford a theoretical value for the coefficient of contraction for such an orifice, provided only its shaping is consistent with the form of jet. For an orifice rounded in this way to the angle θ the ideal coefficient is given by

$$C_0 = \frac{B_1 B_2}{P_1 P_2} = \frac{\pi}{\pi+2 \cos \theta}.$$

It appears, therefore, that rounding is always likely to increase the coefficient of contraction.

When the value of C_0 is correlated with the corresponding value of y from (ii.) we obtain some idea of the effect of

slight rounding. For a half-inch slit orifice corresponding values are

y_s	x_s	θ_s	$\frac{C - C_0}{C_0}$
.00017	.0015	10°	.0059
.00058	.0033	15°	.0132

A rounding of half a mil may therefore be sufficient to increase the coefficient of discharge by 1 per cent. This analysis is, of course, not applicable to forms of orifice other than the slit, but there are good reasons to expect that the general nature of the results will not be dissimilar, and the example cited will suffice to emphasize at once the importance and difficulty of obtaining true sharpness in such orifices. In one instance it is recorded * that a "hardly perceptible" rounding of the edge was sufficient to cause an increase of 20 per cent. in the delivery from a circular orifice, and it is probable that in the case of smaller orifices this is the largest systematic cause of disagreement in published results, and accounts for the serious discrepancies between the evidently careful work of such experimenters as Hamilton Smith, Unwin, Lesbros and others. For this reason also, it would seem that theoretical values for the coefficient of discharge are not likely to have any great practical value for the engineer, who must in general rely on the experimental calibration of each individual orifice.

With an orifice which is "perfectly rounded" into the form of a nozzle (*e.g.*, a venturimeter) there occurs no contraction of the jet at all, and the value of C_0 is unity. It is sometimes assumed that contraction is completely suppressed in any orifice shaped so as to form a "smooth curve" finally parallel to the direction of the jet, and that an arbitrary value of the coefficient of velocity then enables the discharge to be calculated with sufficient accuracy. This has no rational or empirical foundation, and may lead to considerable errors. It is possible, for instance, with an orifice shaped in a "smooth curve," and having an axial length three-quarters of its diameter, to obtain a contraction of 10 per cent. in the jet. Moreover, the amount of this contraction is found to depend upon the exact

* Mair, Proc. Inst. C.E. LXXXIV, p. 428.

shaping of the orifice, and no simple relation between the value of C_0 and the axial length of the nozzle can safely be applied.

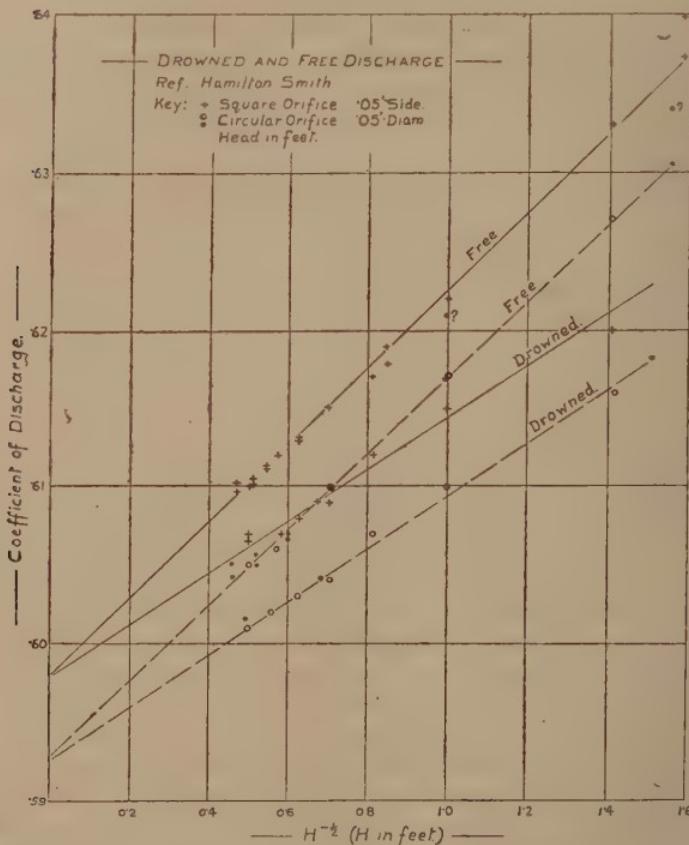
b. *Shape of Orifice.*

For the perfect slit orifice the value of C_0 as afforded by theory is .611. In the absence of theoretical solutions for orifices of other shapes we shall have recourse to experimental results in forming an estimate of the corresponding values. In so doing it will be necessary to exercise some care in the acceptance of individual figures, for there are known to be marked discrepancies between published results, and the coefficients obtained empirically for other shapes have not been very different from those for slit orifices.

Apart from the accidental errors which are associated with hydraulic experiments in general, there are certain special errors of a more or less systematic nature which are peculiar to experiments in orifice flow. Of these the most fruitful source with smaller sizes is imperfect sharpness of the edge of the orifice. Differences in sharpness will introduce systematic errors which, in experiments with a single orifice, will be constant, tending to increase the coefficient of discharge, but not likely to affect the consistency of the results or the general law of systematic changes. With larger orifices and greater heads a more serious source of error is turbulence in approach. This again tends to increase the discharge from a sharp-edged orifice, but its effect is not constant, and it is liable to mask systematic changes. The size and shape of the approach chamber are effective factors in some tests with large orifices, and although an arbitrary correction has usually been applied, the results are of uncertain value. The tendency of any restriction in approach is, of course, to increase the apparent coefficient of discharge. The last common source of error to which attention is drawn is the method adopted for measuring the discharge; for many years the sharp-edged rectangular notch was in almost general use for this purpose. Apart from the fact that the formula used is now known to be merely an approximation applicable over a limited range, the notch itself is intrinsically less sensitive than the orifice as a means of measurement, and is therefore unsuited as a standard for its calibration.

Such errors as these, where the range of coefficients is so small—0·60 to 0·65 as a rule—make it difficult to interpret and reconcile the results of different workers, particularly in cases, not unfrequent, where the conditions of experiment are unrecorded. Further, it will be noted that these errors are mainly systematic, and tend to give high values for the coefficient, so that their effects cannot be eliminated by statistical methods.

Fig. 2.



In interpreting the results of experiments we shall assume that in experiments with water the form of the law governing variations in the coefficient C_d with the head is not affected by the shape of the orifice, so that

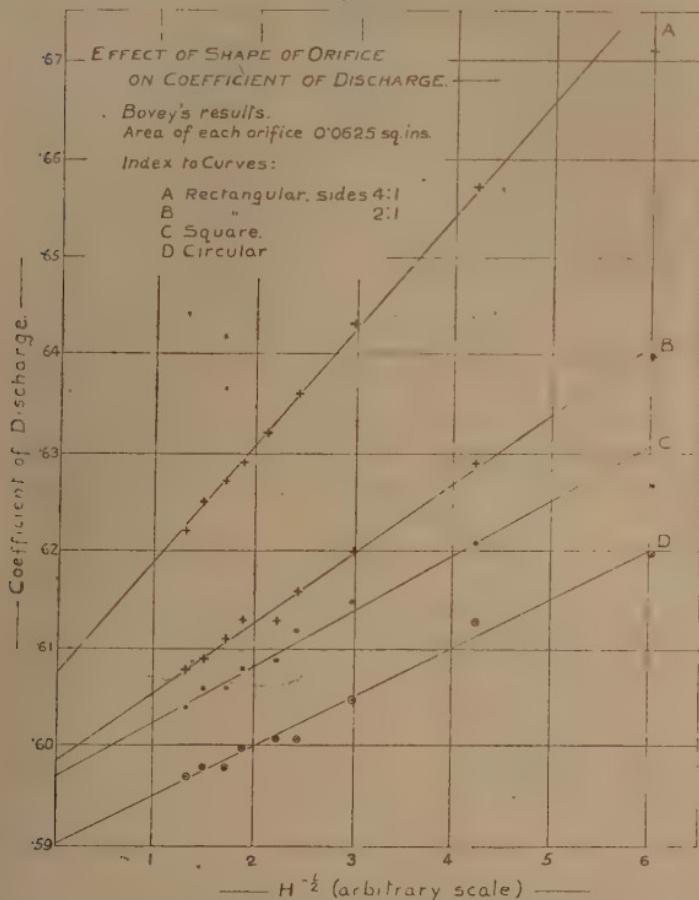
$$C_d = C_0 + \kappa H^{-\frac{1}{2}}$$

This assumption finds support in the results of Hamilton Smith and Bovey, under apparently satisfactory conditions, with the various shapes of orifice referred to in figs. 2

and 3. The limit C_0 determined by extrapolation from such results is the value with which we are concerned.

Recorded experiments with orifices approaching the slit form are rare. The experiments of Poncelet and Lesbros* were made with rectangular orifices of rather large size compared with the dimensions of the approach

Fig. 3 a.



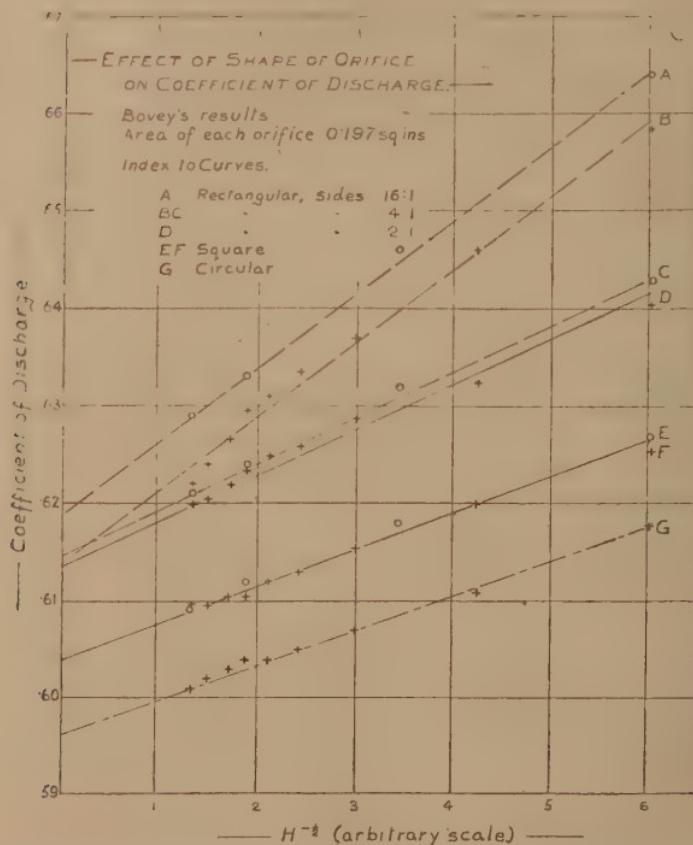
chamber, and since these orifices were in a vertical plane under low heads the value of the results for present purposes can only be regarded as qualitative. Bazin† made determinations with rectangular orifices fitted with side-cheeks to suppress end contraction, but employed a weir as standard of calibration, and did not obtain results sufficiently consistent for comparison. Hamilton Smith and Bovey

* Mem. Acad. Sci. iii. (1832); xiii. (1851).

† Mem. Acad. Sci. xxxii., tr. Trautwine, 1896.

used orifices of different shapes and proportions, and their results (figs. 2, 3) in the case of long, narrow, rectangular slits are seen to be consistent with anticipated variations, and to tend towards a limit which is in reasonable accord with Kirchhoff's ideal value of .61. It is also worthy of note that for such an orifice no accredited value of the coefficient lower than this figure has been published.

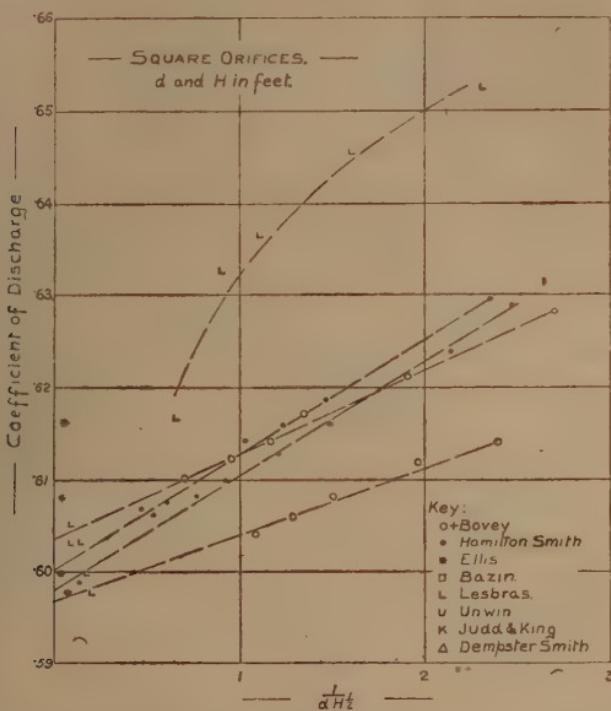
Fig. 3 b.



In the case of rectangular orifices of ordinary proportions, however, there is no general agreement with Kirchhoff's value, and there appears to be sufficient evidence that the theoretical coefficient of discharge is not independent of the shape. The closest practical approximation to the two-dimensional slit is found in the rectangular orifice with side-cheeks, and it is well established (Bidone, 1826; Bazin, 1890) that suppression of the end-contractions

increases the discharge. The analogous result is, of course, well known in the case of rectangular notches and weirs. Moreover, whereas coefficients lower than .61 have not been recorded with orifices approaching to the slit, such lower values have been quite common with those more nearly square, and a coefficient as low as .598 has been obtained with a large square orifice. In figs. 2 and 3 are plotted results obtained by Hamilton Smith and by Bovey and these afford rather striking evidence that the theoretical coefficient continually decreases as the orifice approaches

Fig. 4.



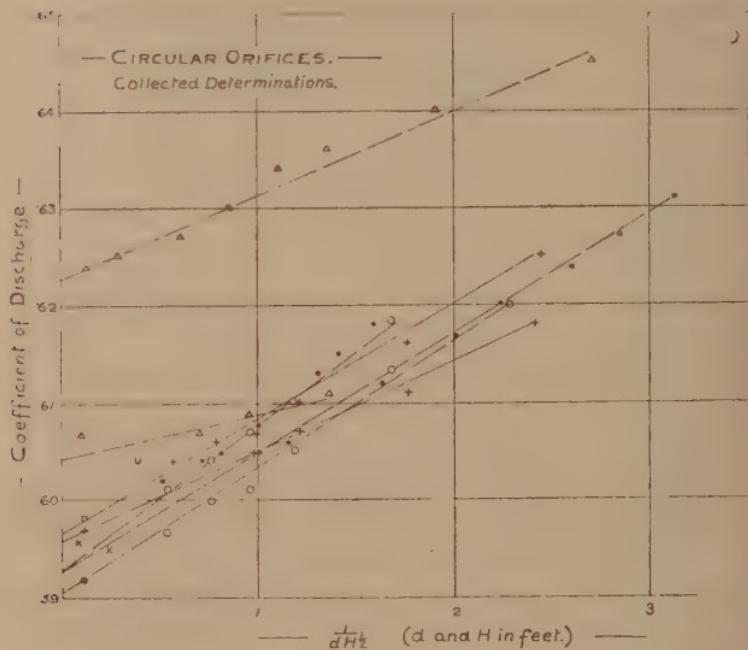
the square form from the slit, and suggest that its value for a square orifice should be about .60. The results deduced by Fanning* for a series of orifices each one foot wide give qualitative support to this conclusion, and the determinations for square orifices from other sources, shown in fig. 4, when account is taken of the general tendency of systematic errors to give high results, show general agreement with a limiting value of .60, or slightly less.

* 'Water Power Engineering' (1887).

For circular orifices a similar comparison of results indicates that the ideal coefficient is again different, and the value suggested by the numerous determinations shown in fig. 5 is close to .59. It is interesting to note that this same limit is also indicated by the experiments of Watson and Schofield * with air through circular orifices.

It seems therefore reasonable to conclude that the value of C_0 for an ordinary "sharp" orifice with restricted approach will depend upon its shape, and will not be less than .61 for

Fig. 5.



a slit, .60 for a square, or .59 for a circular orifice, its agreement with these values depending on its actual sharpness, and tending to improve as the size of orifice increases.

The values of C_0 derived by extrapolation from the results obtained by the author with orifices of various diameters up to one inch, shown in Table I., are reasonably consistent with this conclusion.

* Proc. I. Mech. E., May 1912.

TABLE I.

"Theoretical" Coefficient of Discharge, C_0 .
Extrapolated from experimental results.

Orifice diameter, inches.	Value of C_0 .
0.095	.617
0.302	.612
0.480	.603
0.499	.597
0.602	.593
0.701	.600
0.801	.594
0.907	.597
1.007	.594

Geometry of Approach.

Accepting as basis of comparison the coefficient C_0 for unrestricted approach, the geometry of the approach chamber will be likely to affect the discharge by

- (a) reducing the depth normal to the plane of the orifice;
- (b) restricting lateral approach.

For the slit orifice the effect of these factors is known.

(a) The dimension of the approach chamber normal to the plane of the orifice modifies the contraction according to the relation *

$$\frac{1}{C} = 1 + \frac{1}{\pi} \left(k_0 + \frac{1}{k_0} \right) \log \frac{1+k_0}{1-k_0},$$

where $k_0 = C \frac{a}{b_1}$, in fig. 6 a.

For small values of k_0 this shows that a reduction of depth will cause a decrease in the discharge by an amount given approximately by

$$C = C_0 - 0.12k_1^2 \quad \text{when } C_0 = 0.61,$$

k_1 being the value of $\frac{a}{b_1}$.

* Math. Trip. ii. (1900).

(b) Restriction of lateral approach to a slit tends to increase the area of the contracted jet*, so that

$$\frac{1}{C} = 1 + \frac{2}{\pi} \left(\frac{1}{k_0} - k_0' \right) \tan^{-1} k_0',$$

where $k_0' = C_0 \frac{a}{b_2}$, in fig. 6 b,

and for small values of k_0' , when $C_0 = 0.61$,

$$C = C_0 + 0.12 k_2^2, \text{ where } k_2 = \frac{a}{b_2}.$$

Fig. 6 a.

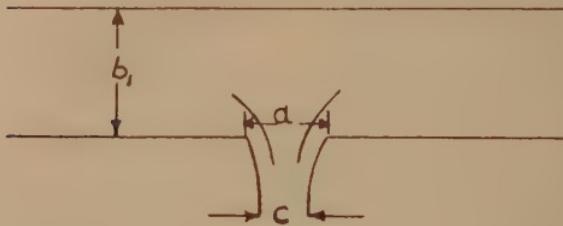
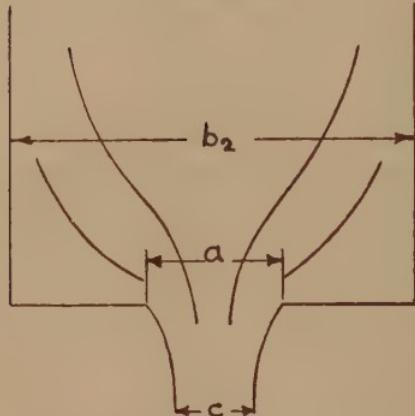


Fig. 6 b.



Effect of Restricted Approach.

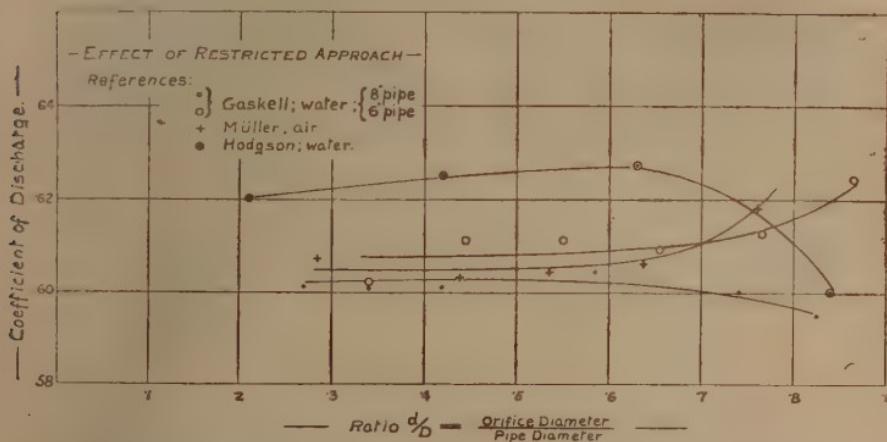
It is not easy to point the analogies for a circular orifice, but there seems to be no physical reason why the general nature of the effects should be different. Experiment has shown that a reduction in depth of water over a horizontal orifice beyond a certain point does, in fact, tend to diminish the coefficient of discharge, but this fact has little practical significance. A matter of considerable

* L. H. Michell, Phil. Trans. p. 405 (1890).

importance, however, bearing on the registration of orifices in pipe-lines, is the effect of lateral restriction in approach.

This effect has been the subject of experimental investigation by several workers with water, steam, and air. In fig. 7 are plotted values of the coefficient of discharge for various ratios of pipe to orifice diameter, calculated on the basis defined on p. 410 from experiments by Müller *, Gaskell †, and Hodgson ‡. Müller's results were obtained with air, the others with water; Gaskell's refer to 8-inch and 6-inch pipes; Hodgson's to pipes $\frac{3}{4}$ -inch diameter and less. Results given by Weisbach § have had to be rejected on account of uncertainty as to the basis on which his coefficients are calculated.

Fig. 7.



When due allowance has been made for the difficulties of experiment, the results plotted in fig. 7 give no evidence of any systematic change in the value of C_0 for values of $\frac{d}{D}$ less than about 0.7. Over this extensive range it would appear that, at any rate for purposes of commercial metering, the coefficient of discharge may be regarded as unaffected by restriction in approach, and this fact may be held to justify the basis on which the coefficient was defined. It is well to note that this constancy is confined to values of the coefficient C_0 . When viscosity has an

* Z. V. D. I. lii. p. 285.

† Proc. Inst. C. E. cciv. p. 11.

‡ Proc. Inst. C. E. xcvi. p. 243.

§ 'Mechanics of Engineering,' p. 825 (tr. 1877).

important effect, the results of Hodgson show that the coefficient is by no means independent of the pipe to orifice ratio.

For values of $\frac{d}{D}$ greater than about 0.7 the tests quoted give divergent results; two give evidence of a rising coefficient, two a falling one, and there is more than a suggestion of increasing uncertainty in the coefficient. This uncertainty is not unexpected; the larger the orifice in a pipe of given diameter, the less the dead-water space on both sides of the diaphragm, the more unstable the conditions in this space and the greater the care required in locating the pressure-tube connexions. It would appear, in fact, that over this range the value of the coefficient is more affected by the exact setting of the diaphragm and arrangement of the pressure tubes than by changes in the ratio $\frac{d}{D}$, and that reliable registration can only be achieved after a careful calibration in which the most exact conditions of operation are reproduced. It is none the less a curious fact that the increase in the value of the coefficient with lateral restriction, which would occur with a slit orifice, should not be more certainly evident in experiments with the circular form.

Methods of Calibration.

Discussion of the various factors controlling orifice flow has led to the conclusion that the value of the coefficient of discharge under any given set of conditions depends upon a basic value C_0 and upon variations due to the physical properties of the fluid in use and to certain conditions of flow. It has been demonstrated that neither by improvement in theory nor by the accumulation of empirical results will it be possible in general to predict with certainty the value of the coefficient for an orifice without individual calibration by experiment. At the same time analysis of the effective factors has indicated the conditions which should be fulfilled in this calibration, and the simplest methods which will cover the required range of flow. These conditions and methods must clearly depend on circumstances.

So far as the constructional factors are concerned, these limit themselves in the case of any one orifice to the

conditions of approach and discharge, and the only satisfactory method of treatment is to ensure that the conditions under which calibration is made shall reproduce in effect the conditions under which the orifice will be required to operate in practice. The care with which these conditions should be reproduced is a matter for consideration in each case, having regard to the results discussed on page 425. It is hardly necessary to point out that an orifice to be employed under conditions of submerged discharge (*e. g.*, in the metering of gases or of pipe-flow) must be calibrated in the same way, and it is clearly important, for the sake of consistency, to reduce the effects of turbulence and pulsation as far as possible both in operation and calibration.

Variations in the coefficient of discharge arising from changes in the hydraulic conditions of flow can generally be covered satisfactorily by a suitable method of calibration. The choice of this calibration will be largely determined by the type of fluid with which the orifice is to be employed.

a. Limpid Liquids.

In the flow of any liquid through an orifice elasticity will, for practical purposes, be ineffective. Under the conditions of submerged discharge surface tension will also be inoperative, so that, in the absence of turbulence, viscosity is the only hydraulic factor which demands attention, and for limpid liquids the value of the coefficient of discharge C_d will follow closely the relation

$$C_d = C_0 + \kappa\eta.$$

For any single orifice the practical law of calibration may therefore be written

$$Q = C_0 a_0 \sqrt{2gH} + cv,$$

where $C_0 a_0$ and c are characteristic of the individual orifice. A comparison of published results, notably those of Hamilton Smith, Bovey, and the author, shows that in the common case of the free discharge of cold water through a sharp circular orifice the empirical formula which best agrees with experiment is

$$C_d = C_0 + \frac{.036}{d\sqrt{H}},$$

where d and H are measured in inches; but this figure is

a mean of rather a wide range of values, and cannot be relied upon for the calibration of any particular orifice. However, the value of the constant $C_0 a_0$ has to be determined experimentally in any case, and only one further test is necessary to determine the other constant c . Thereafter the discharge under any other conditions may be computed from the differential pressure when the kinematic viscosity ν is known. This computation is a simple one, since the form of the expression given above shows that the effect of viscosity is virtually to increase the "theoretical" discharge by an amount which is proportional to the viscosity and independent of the rate of flow. This expression is clearly suited to cases in which the viscosity of the liquid in use is subject to variations, or where the liquid used in calibration is different from that to which the orifice is to be applied. An orifice for use with petrol or with an acid might, for example, be calibrated with water for convenience.

It frequently happens that the viscosity of a liquid flowing through an orifice maintains a reasonably constant value, and under these conditions the law of calibration assumes the still simpler form

$$Q = C_0 a_0 \sqrt{2gH} + q,$$

where q is characteristic of the orifice and liquid and independent of the rate of flow. Calibration at two different heads is still necessary to determine $C_0 a_0$ and q , but the subsequent computation—consisting in the addition of the same small constant q to each "theoretical" discharge—is remarkably simple.

In the free discharge of a liquid to the atmosphere, surface tension also demands attention, and its effect may be estimated by means of the relation given in an earlier paper*. In those rare cases when the correction is considerable an additional test will be necessary in calibration in order to evaluate the three constants, q , $C_0 a_0$, h_s in the relation

$$Q - q = C_0 a_0 \sqrt{2g(H - h_s)}$$

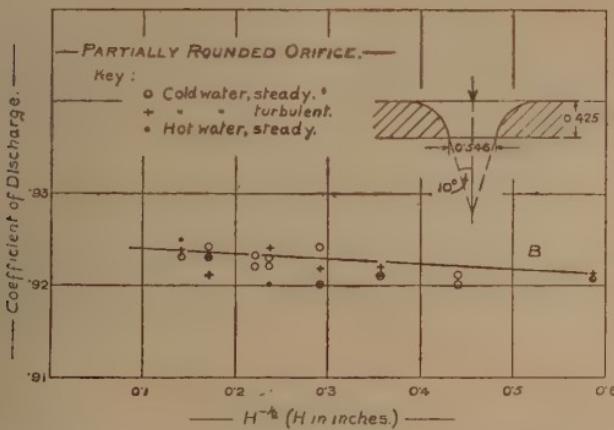
for a liquid where surface tension and viscosity remain sensibly constant. In computing subsequently the discharge corresponding to any observed head this head will first be

* Phil. Mag. p. 853, Oct. 1926.

"corrected" for surface tension by subtracting the constant h_s . From the head so corrected the "theoretical" discharge will be calculated, and this discharge corrected in turn for the effects of viscosity by adding the constant quantity q .

Although these corrections are simple in themselves, it is somewhat troublesome, from the practical point of view, to determine and apply them, particularly in the case of a sharp-edged orifice, for which the calibration is liable to become altered considerably by wear or contamination. The sharp-edged form of orifice is therefore at some disadvantage in the metering of liquids. On the other hand, a nozzle which entirely suppresses the contraction, and is not so liable to wear, is not so convenient to install and replace,

Fig. 8.



and is itself subject to some changes in coefficient at different rates of flow, the sign of q in the expression above in this case being negative. The most convenient form of orifice for practical metering when an accurate and permanent calibration is desired would appear to be one for which the value of q (or κ) vanishes; where, in fact, the suppression of contraction exactly balances the diminution in the velocity of discharge as the criterion varies. An orifice of this form should give a coefficient of discharge sensibly constant in value over a fair range of heads and viscosities for limpid liquids.

An attempt has been made by the author to produce an orifice of this kind, and, after several trials, the form shown in fig. 8 was constructed. When mounted in the base

of a large approach vessel, and discharging to the atmosphere, this orifice gave the results shown in fig. 8 and Table II. From this table it will be seen that the coefficient

TABLE II.
Special Rounded Orifice.
Diameter 0·546 inch.

A. Time for head to fall from 55 inches to 5 inches in tank about 2 ft. 6 in. diameter.

Conditions.	Temperature, ° C.	Time, seconds.
Quiescent	14	1149·8 1150·1
Turbulent	14	1150·2 1150·5
Quiescent	63	1151·4 1151·0

B. Determinations at constant heads.

Head, inches.	Value of C_d .
21·1	.923 .922
5·15	.921 .920

of discharge with water is practically independent not only of changes in head from 6 inches to 5 feet, but also of changes in viscosity due to temperature variations from 10° to 60° C. Furthermore, this orifice possesses another valuable characteristic from the practical point of view—its coefficient is practically unaffected by turbulence in approach. If, therefore, orifices of this form could be constructed without difficulty they would appear to be invaluable for metering purposes. Unfortunately, in the course of the trials which led eventually to this form it became clear that, even with rounded orifices, the details of curvature and construction exercise a considerable influence on the coefficient, so that special care would be required in the reproduction of orifices of other sizes.

Moreover, the form of orifice which gives this constancy of coefficient under conditions of free contraction does not do so when contraction is partially suppressed, as in a pipe, and a special shape would be necessary for each ratio of orifice to pipe-diameter. Once the labour of initial testing had been carried out, however, there seems to be no reason why a "constant coefficient" form of orifice should not be produced with suitable templates for conditions of either free or suppressed contraction.

b. *Viscous Liquids.*

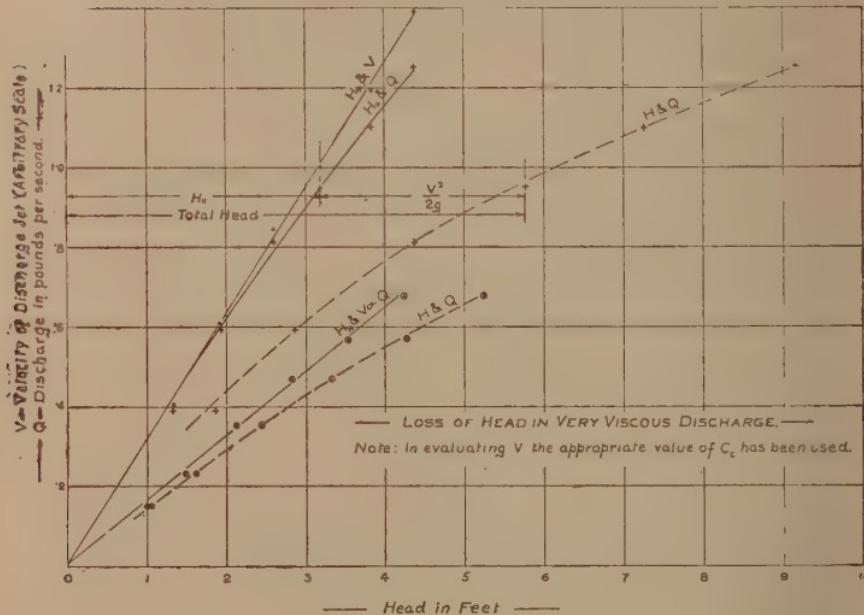
The methods of calibration detailed above apply only to the range of flow over which the coefficients of velocity and contraction change in an approximately linear way with the value of the criterion η . This is true only for low values of this criterion such as are encountered in the flow of water and other liquids of low viscosity. As the value of the criterion η increases beyond this range, neither the coefficient of velocity nor (where effective) the coefficient of contraction follows such a simple law, and satisfactory calibration of a sharp-edged orifice under these conditions is a tedious matter. Furthermore, the actual curve connecting the coefficient of discharge with values of η has been found, at any rate for discharge to atmosphere, to be not independent of the liquid in use, so that changes in viscosity are liable to invalidate a calibration curve. On the other hand, the coefficient of velocity over the whole range of flow appears to follow fairly simple and systematic variations, and it would seem, therefore, that the most satisfactory course to follow in practice over the non-limpid range is to ensure that the shaping of the orifice is such as to suppress contraction, and so to confine consideration to changes in the coefficient of velocity. The extent to which an orifice would need rounding to satisfy this condition depends upon the liquid and size of orifice. For high values of η , contraction, even with a sharp-edged orifice, is practically entirely suppressed, and the more viscous the liquid and the smaller the orifice and rate of flow the less the amount of rounding required for the purpose. Assuming that this condition is fulfilled, the calibration is not difficult.

For a liquid of given viscosity the loss of head incurred during discharge from an orifice is proportional to the

velocity at the vena contracta. This fundamental assumption has been justified in the case of limpid flow, and fig. 9 furnishes experimental confirmation for very viscous flow where contraction is almost or entirely absent. It follows, by dimensional reasoning, that the loss of head may then be expressed as $H_x = c\eta \frac{V^2}{2g}$, and the velocity of discharge is related to the head according to the expression

$$H = \frac{V^2}{2g} + \frac{cv}{2gd} \cdot V.$$

Fig. 9.



When contraction of the jet is entirely suppressed, the law of calibration is, therefore,

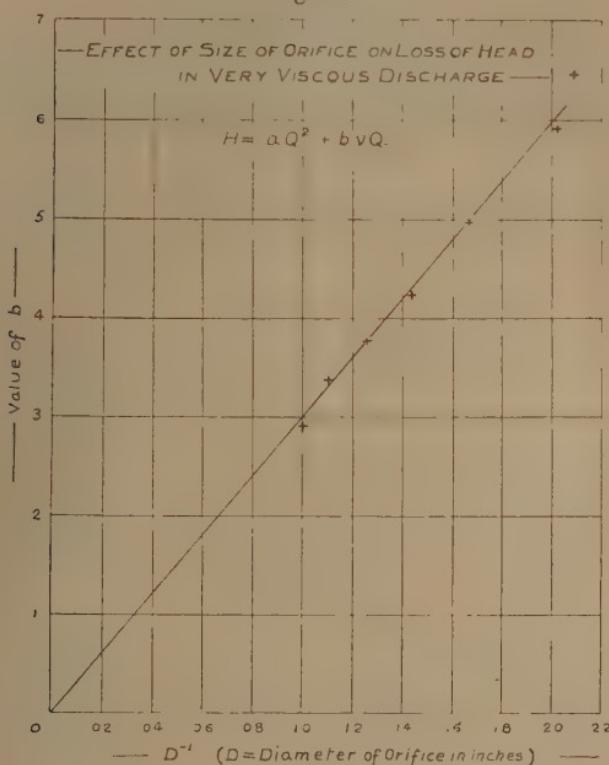
$$H = \frac{Q^2}{2ga_0^2} + bVQ,$$

where b is a dimensional quantity characteristic of and constant for any individual orifice. For a series of similar orifices the value of b should vary inversely with the diameter, and when there is no contraction of the jet this

relation is not likely to be very sensitive to small differences in workmanship. In fig. 10 are plotted values of b deduced from experiments with orifices from 0·48 to 1·0 inch diameter which confirm this relation, and thereby the reasoning on which it is based.

The calibration of an orifice under these conditions consists merely in the measurement of its area a_0 and in the determination of the constant b (or $b\nu$ if viscosity is invariable) by a single test which may best be made with a

Fig. 10.



viscous liquid under a low head. Subsequently each computation of discharge corresponding to an observed value of the head would involve the solution of a quadratic equation in Q , but this may be avoided by the use of a simple calibration chart.

In applying this, or indeed any, method of calibration to an orifice for use with viscous liquids, it is important to realize that the more viscous the liquid the more sensitive

will the registration be to changes in viscosity, and as a rule, in practice, the viscosity of thick liquids is itself very sensitive to changes in temperature. Under such conditions, therefore, the accuracy of registration of an orifice or similar meter is limited not so much by errors of calibration as by uncertainty of the effective viscosity. A rise in temperature of $5^{\circ}\text{C}.$, for example, might increase the coefficient of discharge for a thick oil by 50 per cent., and yet not affect the flow of water by .2 per cent.

c. Gases and Vapours.

In gaseous discharge through an orifice, viscosity and elasticity are both effective, and the coefficient of discharge for conditions under which each effect is small is given by

$$C_d = C_0 + \alpha\eta - \beta \frac{r}{\gamma}$$

with the notation already adopted, and the flow may be expressed in the form

$$Q = q + C_0 \alpha_0 \sqrt{2gH} \left(1 - c \frac{r}{\gamma} \right),$$

where q represents the effect of viscosity, as in the case of liquid flow, and the factor $\left(1 - c \frac{r}{\gamma} \right)$ represents the effect of compressibility.

In this case a complete calibration would involve three separate tests to determine q , $C_0 \alpha_0$, and c , and the subsequent computation of Q would be made by correcting C_d , in the first place, for compressibility, and later adding to the calculated discharge the constant q for viscosity correction. In calibration the constants q and $C_0 \alpha_0$ could be determined for convenience by means of tests made with water, but the third test, to determine the elastic effect, could only be made with a gas. This fact adds considerably to the trouble of calibration, and if one test has to be made with a gas there is little to be gained by using water in the other two. Fortunately, however, the correction for compressibility is generally so small that an approximate general formula can be employed without the possibility of a serious error, and in many cases it will be found that the correction itself is negligible.

For a rounded orifice, or nozzle, the correction can be calculated with confidence, and under normal conditions of metering $c = \frac{3}{4}$. For air at or near atmospheric pressure

the corresponding correction is less than 1 per cent. so long as the pressure difference across the orifice does not exceed $7\frac{1}{2}$ inches of water-gauge, and for saturated steam at a pressure of 200 lb. per sq. inch the corresponding pressure difference is about 6 inches of mercury. With a sharp-edged orifice partial suppression of the contraction has the effect of reducing the resultant correction, so that $c = \frac{1}{6}$ approximately, and the error involved by neglecting compressibility altogether is less than 1 per cent. with air at atmospheric pressure so long as the water-gauge is less than 34 inches, and with steam at 200 lb. per sq. inch pressure so long as the pressure difference does not exceed $27\frac{1}{2}$ inches of mercury. The fact that the correction for compressibility is so much smaller with a sharp-edged orifice places it at some advantage over rounded forms for use with gases ; it is true that the viscosity correction will usually be greater, but this is determinable by tests with water. It would appear that as a rule, with either form, the calibration of an orifice for use with a gas or vapour can be carried out satisfactorily by means of water, and if any correction for compressibility is necessary the values of c quoted above will give results sufficiently accurate for all ordinary purposes.

In arranging the calibration by means of water it is well that the tests should cover generally the same range of values of η as will obtain when the orifice is in use. For any one orifice corresponding heads are given by the formula

$$\frac{H_1}{H_2} = \left(\frac{v_1}{v_2} \right)^2.$$

If, for example, the orifice is required for air under approximately atmospheric conditions, the head under which it should be calibrated to correspond to a water-gauge p is approximately $5p$, which will normally be a reasonable head, and enable simple arrangements to be made. Unfortunately, the viscosity of steam under the conditions which prevail in practice does not seem to have been evaluated experimentally, so that it is not possible to give with confidence the corresponding heads of water for an orifice to be employed as a steam-meter.

XLVII. The Nature of the General Polarization Effect in Aromatic Molecules. By W. A. WATERS, M.A., Ph.D., Lecturer in Chemistry, University of Durham (Durham Division)*.

IN the following communication an attempt is made to correlate reaction velocity measurements, obtained with aromatic compounds, with electrical dipole moments, with the object of elucidating further those intramolecular forces which seem to be characteristic of aromatic ring systems.

Bradfield and Jones (J. Chem. Soc. pp. 1008, 3073, 1928), utilizing the equation

$$k = PSZe^{\frac{-E}{RT}} \dots \dots \dots \quad (1)$$

for representing the velocity of any substitution reaction, have shown that it is the energy of activation (E) of any aromatic molecule which is primarily altered by the presence of a substituent group, so that in consequence the equation

$$RT \cdot \log (K_{\text{subs.}}/K_{\text{unsubs.}}) = E_{\text{unsubs.}} - E_{\text{subs.}} \dots \quad (2)$$

may be used for comparing the reaction velocities of substituted with those of unsubstituted compounds.

This equation is closely allied to that previously given by Shoesmith and Slater (J. Chem. Soc. p. 216, 1926) :—

$$\log K_{\text{subs.}} = \log K_{\text{unsubs.}} + g + a + s \dots \quad (3)$$

where g , a , and s , are arbitrary factors representing the magnitudes of the general, alternating, and steric effects respectively of the substituent group.

Of these factors, that representing the steric effect can only be observed when the substituent group is in the ortho position to the point of attack, and even then may be exerted only under certain special circumstances (cf. Olivier, *Rec. trav. chim.* xlviii. p. 227, 1929). It may perhaps be identified more closely with the steric factor (S) of equation (1). The alternating polarity effect (a) in contrast can be observed most decidedly with both ortho and para substituent groups. As, however, it has been characterized as a tautomeric (electromeric) transformation (Chemical Society, Annual Reports, p. 140, 1926, p. 151, 1927) it may not be noticed to any great extent in the case of a *meta*

* Communicated by Prof. Irvine Masson, D.Sc.

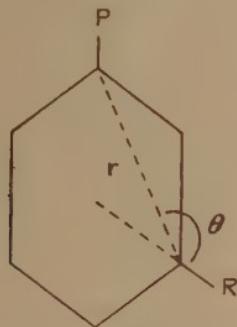
substituent group, as this would not be in a position conjugated to the point of attack.

The general polar effect, however, is an *inductive disturbance* (Chemical Society, Annual Reports, *loc. cit.*) which will influence the rate of any reaction, whatever the position of the modifying substituent group within the molecule. This effect can be correlated with the possession by the modifying substituent group of a dipole moment.

For, if μ be the dipole moment of the substituent group $-R$, then the induced potential at any other point P within the molecule will be $\mu \cos \theta / r^2$, and in consequence any moveable electron (or ion) at the point P will require for activation an energy

$$E_{\text{subs.}} = E_{\text{unsubs.}} + k \cdot \mu \cos \theta / r^2 \quad \dots \quad (4)$$

(according to the vector sign of the dipole moment).



It follows that, for any fixed orientation relationship between P and $-R$, $\log \left(\frac{K_{\text{subs.}}}{K_{\text{unsubs.}}} \right) \propto \mu$, under conditions in which only the general polarization effect has an appreciable magnitude, whatever the nature of the substituent group $-R$. That the dipole moment has a magnitude approximately proportional to the change of energy of activation of aromatic molecules on substitution may be seen from the following typical tables of correlations of reaction velocity measurements with electrical dipole moments. Meta substituent groups have been examined in order to eliminate the alternating and steric influences as much as possible, following the hypothesis outlined above.

In considering the degree of correspondence between the functions $\log \frac{K_s}{K_u}$ and μ , it must be remembered not only that reaction velocity constants may be uncertain to a few

units per cent., but also that the recorded values of the dipole moments are at present of rather a tentative nature, especially with respect to groups with small dipole moments, as even the theoretical basis of the methods for their computations is still indeterminate (*cf.* Estermann, *Z. Physikal. Chem.*, pp. 134-160, 1928 i.; Ebert, Eisenschitz, and von Hartel, *ibid.* pp. 94-114).

TABLE I.

Dissociation Constants of *m*-substituted Aromatic Acids at 25° C.

Substituent.	K _{Ostwald.}	$\log \frac{K_s}{K_u}$.	$\mu \times 10^{18}$ e.s.u.	$\frac{\log K_s / K_u}{\mu \times 10^{18}}$.
-NO ₂	3.48×10^{-4}	+0.72	-3.75*	-0.21
-Cl	1.55×10^{-4}	+0.37	-1.58*	-0.24
-Br	1.45×10^{-4}	+0.32	-1.56*	-0.20
-CH ₃	5.6×10^{-6}	-0.07	+0.43*	-0.17
-COOCH ₃ ...	1.28×10^{-4}	+0.29	-1.8 °	-0.16
-NH ₂	1.67×10^{-5}	-0.60	+1.6 °	-0.37
-COOH	2.9×10^{-4}	+0.64	?	(-0.36)
-OCOCH ₃ ...	1.81×10^{-4}	+0.80	?	(-0.16)

TABLE II.

Dissociation Constants of *m*-substituted Primary Aromatic Bases at 25° C.

Substituent.	K _{Ostwald.}	$\log \frac{K_s}{K_u}$.	$\mu \times 10^{18}$ e.s.u.	$\frac{\log K_s / K_u}{\mu \times 10^{18}}$.
-NO ₂	4.1×10^{-12}	-2.05	-3.75*	+0.55
-Cl	3.45×10^{-11}	-1.12	-1.58*	+0.71
-Br	3.8×10^{-11}	-1.08	-1.56*	+0.69
-COOCH ₃ ...	4.4×10^{-11}	-1.02	-1.8 °	+0.57
-COOH	1.2×10^{-11}	-1.58	?	(+0.88)
-OH ₃	5.5×10^{-10}	-0.07	+0.43	-0.18

In the above tables the dissociation constants have been taken from Landolt-Börnstein's 'Tabellen.' The dipole moments marked * are taken from Höjendahl ('Nature,' exvii. p. 892, 1926), and those marked ° from Estermann (*loc. cit.*). Where indicated by the query (?) no experimental measurement of the electrical dipole moment of the corresponding aromatic compound has yet been made,

but for the purposes of these computations it has been assumed provisionally that the dipole would be associated with the $=\text{C}=\text{O}$ group in each case, and that it would have the magnitude of about 1.8×10^{-18} e.s.u. as in the case of methyl benzoate.

A sign has been assigned to the dipole moment according to whether the electrical field produced at the point of reaction (P) corresponds with a positive or negative induced general polarity (I), following the standard nomenclature of Ingold (Chemical Society, Annual Reports, *loc. cit.*).

TABLE III.

Rate of Hydrolysis of *m*-substituted Benzyl Chlorides.
(Olivier, *Rec. trav. chim.* xli. p. 646, 1922.)

Group.	$\mu \times 10^{18}$ e.s.u.	A.....		B.....	
		K_s/K_u .	$\log K_s/K_u$ $\mu \times 10^{18}$.	K_s/K_u .	$\log K_s/K_u$ $\mu \times 10^{18}$.
$-\text{CH}_3$	+0.43	1.39	+0.34	1.30	+0.27
$-\text{Cl}$	-1.58	0.237	+0.40	0.137	+0.55
$-\text{Br}$	-1.56	0.215	+0.43	0.132	+0.58
$-\text{NO}_2$	-3.75	0.09	+0.28	0.057	+0.33
$-\text{COOH}$...	?	0.235	(+0.35)	0.170	(+0.43)

TABLE IV.

Rate of Hydrolysis of *m*-substituted Benzyl Bromides.
(From Shoesmith and Slater, J. Chem. Soc. 216, 1926.)

Temp.	Group.	$\mu \times 10^{18}$.	$(g-a)$.	$\frac{(g-a)}{\mu \times 10^{18}}$.
60° C.	$-\text{OCH}_3$	+0.8 °	>6.2	+0.78+
60° C.	$-\text{CH}_3$	+0.43	0.40 ..	+0.92
76° C.	$-\text{Cl}$	-1.58	-0.82	+0.52
76° C.	$-\text{Br}$	-1.56	-0.82	+0.53
76° C.	$-\text{NO}_2$	-3.75	-1.72	+0.45
76° C.	$-\text{COOH}$?	-1.12	+0.59

NOTE.—The value $(g-a)$ given by Shoesmith and Slater is equal to $\log K_s/K_u$ for the meta substituent groups.

In each of these widely differing sets of data the variation of the ratio $\frac{\log K_s/K_u}{\mu}$ is within the present limits of

accuracy of the experimental measurements. Both the reaction velocities and the dipole moments can vary widely, and not necessarily uniformly, with changes of physical conditions (*cf.* Estermann, *loc. cit.*, McCombie, Scarborough, and Smith, J. Chem. Soc. p. 803, 1927), and it must be remembered that the respective conditions chosen for the measurement of the reaction velocities and of the electrical dipole moments may not be strictly comparable.

In contrast to the above results, no such close relationship can be traced between the reaction velocity change on substitution and the dipole moment when the substituent group is in either the ortho or the para relationship to the point of reaction in the aromatic molecule. This may well be illustrated from the following table, which is typical of a wide range of experimental data that has been analysed in the same way.

TABLE V.
Dissociation Constants of Substituted Aromatic
Acids at 25° C.

Group.	$\mu \times 10^{18}$.	Para Series.		Ortho Series.	
		K _{Ost.}	$\frac{\log K_s/K_u}{\mu \times 10^{18}}$	K _{Ost.}	$\frac{\log K_s/K_u}{\mu \times 10^{18}}$
-NO ₂	-3.75	3.93×10^{-4}	-0.21	6.5×10^{-3}	-0.53
-OH	+1.73	2.9×10^{-5}	-0.21	1.06×10^{-3}	+0.70
-COOH ...	?	1.5×10^{-4}	-0.20	1.26×10^{-3}	-0.70
-CH ₃	+0.43	4.3×10^{-5}	-0.44	1.25×10^{-4}	+0.66
-OCOCH ₃ .	?	8.9×10^{-5}	-0.72	3.27×10^{-4}	-0.39
-NH ₂	+1.6	1.2×10^{-5}	-0.46	1.06×10^{-5}	-0.50
-OCH ₃	+0.8	3.2×10^{-5}	-0.39	—	—
-COPh.....	-2.5	—	—	3.7×10^{-4}	-0.19
-Cl	-1.58	1.3×10^{-3}	-0.82	1.32×10^{-3}	-0.82
-Br	-1.56	—	—	1.45×10^{-3}	-0.86
-COOMe ...	-1.8	—	—	6.56×10^{-4}	-0.24

This would seem to support the supposition that the dipole moment can only be correlated with the *general* polarization effect.

The fact that a less pronounced, but detectable, correlation can be traced in several series of measurements of para substitution derivatives may perhaps be taken as evidence in support of the frequently expressed view that the general polarization effect is more powerful than the

alternating polarity effect (Berger, *Rec. trav. chim.* xlvi. p. 545, 1927) in modifying reaction velocities. In the case of ortho substitution compounds too many influences modify reaction velocity for any simple correlations to be observable.

From experimental evidence alone no estimate can be given for the magnitude of the general polarization effect in the ortho or the para position in comparison with that measurable in the meta position, though a rough theoretical conception of this relationship can be deduced from consideration of equations (3) and (4), from which it follows that :—

$$g_o : g_m : g_p = \cos \theta_o / r_o^2 : \cos \theta_m / r_m^2 : \cos \theta_p / r_p^2 . \quad (5)$$

where θ and r are respectively the angles subtended, and the distances of the centres of the dipoles from the point of attack (P).

For the influence of dipolar groups attached directly to the aromatic ring upon other groups also attached directly to the ring this relationship simplifies down to :—

$$g_o : g_m : g_p = \frac{1}{2} : \frac{1}{2\sqrt{3}} : \frac{1}{4}.$$

In simple cases therefore the general polarization effect has a constant sign and diminishes regularly in magnitude with the distance of the substituent group from the point of reaction within the molecule. This is in complete agreement with the fundamental conception of the nature of the general polarization effect, as previously advanced by many authors from purely qualitative experimental evidence.

Summary.

The general polarization effect in aromatic molecules may be correlated with the dipole moment of the substituent group.

By utilizing the relationship $\log K_s/K_u \propto \mu$ the relative orders of magnitude of the reaction velocities of all meta substituted aromatic compounds can be predicted from a knowledge of the electrical dipole moments of the substituent groups and vice versa. With para substituted compounds the prediction is considerably less certain, and with ortho substituted compounds no such prediction can be made.

The hypothesis advanced is in complete harmony with earlier qualitative theories.

XLVIII. On the Interpretation of X-Ray Crystal Photographs.—Part II. Complete Rotation Photographs. By Wm. H. GEORGE, M.Sc., Ph.D., F. Inst. P., Assistant Lecturer in Physics in the University of Leeds*.

[Plate X.]

Summary.

The paper describes a simple mathematical instrument which directly interprets principal-axis, complete rotation photographs of cubic, tetragonal, hexagonal, and trigonal crystals. A rotating cursor is clamped upon one scale, at a graduation depending upon the size of the unit-cell and the wave-length of the X-rays. The line of the cursor then intersects two other scales at a series of points, each pair of which corresponds to the crystal indices and the row-line reading upon the film where the "spot" of the photograph is to be sought.

In combination with the *grid-method* (Part I.) of measuring X-ray photographs, the method is entirely independent of the type and dimensions of the spectrometer, the wave-length of the X-rays, or the size of the unit-cell of the particular substance, and it involves no graphical construction or calculation.

Partial applications of the work are described, and some tables of constants are given for use in connexion with reciprocal lattice methods for interpretation of rotation photographs.

IN the previous paper⁽¹⁾ a general method was described for measuring any kind of X-ray crystal photograph taken on any type of spectrometer. The next stage in the interpretation of the photograph is the identification, *i.e.*, determination of the Miller indices (*hkl*), of the sets of crystal planes which have caused the diffraction effects. For this purpose each type of photograph has to be treated separately. The procedure is of course to calculate all possible theoretical coordinates, using the known geometry of crystal structure, and to compare the results with the observed experimental values. In general the equations are complex⁽²⁾. For example, the Bragg angle θ_n for an *n*th order of reflexion of X-rays of wave-length λ from the (*hkl*) planes of any hexagonal crystal of cell dimensions a_0 and c_0 is given by:—

$$n\lambda = \frac{2a_0}{\sqrt{4/3(h^2 + hk + k^2) + (la_0/c_0)^2}} \sin \theta_n. \quad (1)$$

Graphical methods of obtaining the theoretical values have been used, and an admirable summary of them has

* Communicated by Prof. R. Whiddington, F.R.S.

been given by Schiebold⁽³⁾. The objection to graphical methods is that they give results applicable to only one particular substance. In the present paper a simple mathematical instrument is described which directly interprets certain *types* of complete rotation photographs for all possible cases.

Complete Rotation Photographs.

The interpretation of rotation photographs is much facilitated by the use of the reciprocal lattice theory developed by Ewald⁽⁴⁾, Polanyi⁽⁵⁾, Schiebold⁽⁵⁾, Weissenberg⁽⁶⁾, Mauguin⁽⁶⁾, and Bernal⁽⁷⁾, and the instrument to be here described depends upon the use of this theory.

We will assume that the photograph has been taken by rotating a single crystal continuously through 360° about an axis perpendicular to the incident pencil of mono- (or di-) chromatic X-rays, the diffracted X-rays being recorded photographically on a coaxial cylindrical film or on a plane plate normal to the undiffracted X-ray pencil. We will assume further that, since reciprocal lattice theory is to be used in interpreting the photograph, one of the Bernal⁽⁷⁾ charts (I. for a plane plate or II. for a cylindrical film) has been used to prepare the grid.

Notation.—Under these conditions, if cylindrical coordinates (ξ, ζ, ω) referred to the axis of rotation are used, the angular coordinate ω is indeterminate, since the orientation of the crystal when it is producing a given "spot" is incompletely known. The other two coordinates ξ and ζ are either coordinates of the point in the reciprocal lattice corresponding to the crystal plane which has produced the spot on the rotation photograph, or they are the coordinates of the spot read off from the photograph. In the latter case ξ is the reading of the *row-line* and ζ is the *layer-line* ("schichtlinie") reading. In the plate (fig. 3) of Part I.⁽¹⁾ the sets of curves are the row-lines and the vertical straight lines are layer-lines. These latter would have been hyperbolæ if a plane plate had been used.

a or c = length of an edge of the unit cell,

= primitive translation along the a or c axes in the crystal lattice.

$A = \lambda/a$ or $C = \lambda/c$ are the corresponding primitive translations of the reciprocal lattice.

λ = wave-length of the monochromatic X-rays used.

hkl = Miller indices of the sets of crystal planes.

We then have^{(6), (8)} for a *cubic* or *tetragonal* crystal rotated about the principal axis (*c*) :—

$$\xi = \frac{\lambda}{c} \{ h^2 + k^2 \} = C \{ h^2 + k^2 \}^{\frac{1}{2}} \quad \dots \dots \quad (2)$$

and $\zeta = lC \quad \dots \dots \dots \dots \dots \dots \dots \quad (3)$

For a *trigonal* or *hexagonal* crystal referred to three orthohexagonal axes *a*, $b=a\sqrt{3}$, and *c*, and rotated about the *c* axis (*c*) :—

$$\xi = A \left\{ h^2 + \frac{k^2}{3} \right\}^{\frac{1}{2}} \quad \dots \dots \dots \dots \quad (4)$$

$$\zeta = lC \quad \dots \dots \dots \dots \dots \dots \dots \quad (5)$$

For the most general type of rotation of a *cubic* crystal about a $[uvw]$ zone-axis we have

$$\xi = C \left\{ h^2 + k^2 + l^2 - \frac{hu + kv + lw}{u^2 + v^2 + w^2} \right\}^{\frac{1}{2}} \quad \dots \dots \quad (6)$$

$$\zeta = \frac{C(hu + kv + lw)}{(u^2 + v^2 + w^2)^{\frac{1}{2}}} \quad \dots \dots \dots \dots \dots \dots \quad (7)$$

Also under these conditions we have for all planes on the *n*th layer-line

$$hu + kv + lw = n \quad \dots \dots \dots \dots \quad (8)$$

The most commonly employed zone-axes are the $[110]$ and the $[111]$, when equations (6) (7) and (8) reduce to :—

For a *cubic* crystal rotated about the $[110]$ zone axis,

$$\xi = C \left\{ l^2 + \frac{(h-k)^2}{2} \right\}^{\frac{1}{2}}, \quad \dots \dots \dots \quad (9)$$

$$\zeta = \frac{C}{\sqrt{2}}(h+k), \quad \dots \dots \dots \dots \quad (10)$$

and $h+k=n$ for all planes on the *n*th layer line $\dots \dots \dots \dots \quad (11)$

For a *cubic* crystal rotated about the $[111]$ zone-axis,

$$\xi = C \left\{ h^2 + k^2 + l^2 - \frac{(h+k+l)^2}{3} \right\}^{\frac{1}{2}}, \quad \dots \dots \quad (12)$$

$$\zeta = \frac{C}{\sqrt{3}}(h+k+l), \quad \dots \dots \dots \dots \quad (13)$$

and $h+k+l=n$ for all planes on the *n*th layer-line. $\quad (14)$

From an examination of these equations two features, of great importance from the present point of view, are apparent. Firstly, the quantities inside the brackets are quite independent of the wave-length of the monochromatic X-rays used, of the axial ratio or absolute dimensions of the unit cell of the particular substance, and of the distance from the crystal to the plane plate or cylindrical film. They represent, then, universal constants * for the particular crystal system or type of photograph. Secondly, if we assume that these constants have been worked out for all possible crystal planes (*i.e.*, integral values of hkl) which may occur in practice, then the equations are all of the very simple form $N = MK$. It is clear, then, that a machine which would solve this type of equation would directly interpret the types of photograph considered.

Theory of Instrument.

It would appear that where simplicity in the final result is desired, the best basis for such a machine is a nomographical solution of the equation. The principles of nomography are treated in standard works⁽⁹⁾, and the solution (fig. 1) used here need only be described.

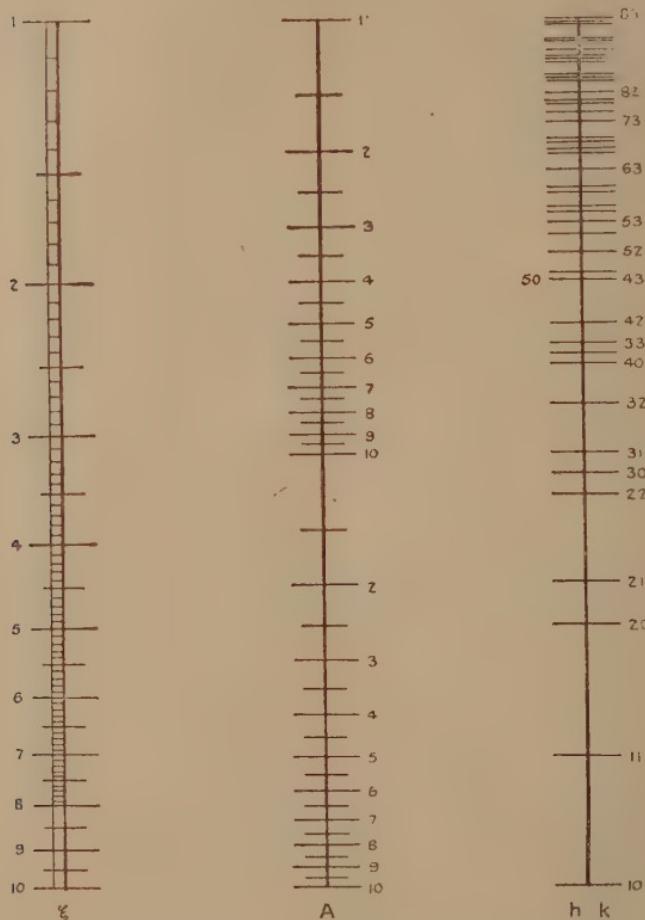
Three parallel straight lines of equal length are drawn perpendicular to a common base-line (not shown in fig. 1). The central line is midway between the other two, which may be *any* convenient distance apart. The left-hand line, marked ξ , is graduated logarithmically from 1 to 10, starting from unity at the *top*. The middle line is similarly graduated on a half-scale from 1 to 10 and 10 to 100, starting with unity at the *top*. The right-hand line is graduated according to the type of photograph to be interpreted. For example, for all cubic and tetragonal (*c*) axis rotation photographs it is graduated with the logarithms of the constants $\{h^2 + k^2\}^{1/2}$ given in the third column of Table I. The scale of these graduations is the same as on the left-hand line, *i.e.*, from 1 to 10, but starting with unity at the *bottom*. The graduation is best done with a logarithmic ruler, so that graduations are made opposite the reading on the ruler

* Hull (Phys. Rev. x, pp. 661-696 (1917), has given tables of constants for the cubic system for the interpretation of powder photographs from spacing considerations. The spacing equations⁽²⁾ for all other systems contain the axial ratios involved in terms together with with indices (hkl). Universal constants cannot therefore be calculated (*cf.* equations (1) and (4) of the present paper). The Hull constants for the cubic system differ from those given here, since the present ones are calculated for use with reciprocal lattice theory.

corresponding to each number in the third column of Table I., and each graduation is marked with the indices hk given in the first column.

The complete diagram (fig. 1) then represents all possible numerical solutions of equation (2), in that any straight line

Fig. 1.



Tetragonal or cubic crystal rotated about principal axis.

passing through a graduation on the right-hand scale cuts the other two scales at points corresponding to some pair of possible values of ξ and A in equation (2). This type of nomographical solution of the equations forms the basis of the instrument shown in Pl. X.

Description of Instrument.

Three wooden scales with white xylonite facings carrying graduations, as described, were mounted on a drawing-board in the relative positions shown in fig. 1. On each scale the total length of graduations is 20 inches, so that the middle and left-hand scales can be ruled on a machine used to make 20-inch slide-rules. The right-hand scale, which can be changed according to the type of photograph, is ruled by hand according to the tables. On the centre scale, which is lower than the two outer ones, a brass fitting slides, and can be clamped by the lever shown on the right-hand side in Pl. X. at any desired position along the scale. This brass fitting carries a strip of transparent xylonite, ruled with a fine black line, to act as a cursor. The upper circular part of the brass fitting is held to the lower part by a spring, so that, although the cursor can be rotated about any point on the middle scale, it will also remain set in any desired position across the scales.

Use of Instrument.

For any type of complete-rotation photograph here discussed the left-hand and middle scales of the instrument (Pl. X.) are the same. The right-hand scale shown in the figure is the one used for photographs of cubic or tetragonal crystals rotated about the principal axis (c). For such photographs the brass fitting is clamped at the lower reading on the middle scale corresponding to the value of A ($=\lambda/a$), where λ is the wave-length of the monochromatic X-rays used, and a is the length on edge of the square base of the unit cell. Then for all spots on the zero layer-line the index l is zero, or in general l is the same as the number of the layer-line. The other two indices hk are got by merely rotating the cursor through the graduations on the right-hand scale. Then the intersection of the cursor with the left-hand scale gives for each pair of indices hk the row-line reading ξ , where the photograph must be examined for a possible crystal reflexion.

Great care must be taken in interpreting the zero layer-line, since the radiation used is often dichromatic, *i.e.*, the intensity of K_β radiation is quite great enough, compared with that of the K_α , to give spots from well-reflecting planes. For all except the zero layer-line the K_α and K_β reflexions lie on different layer-lines. Since in general the K_α and K_β reflexions lie on different row-lines, confusion can be

avoided by following the row-line of each spot on the zero layer-line, until it cuts some other layer-line. It is also easily possible to confuse the K_β reflexion of a plane with the K_α reflexion of some other plane. This coincidence of row-lines depends, of course, upon the particular values of λ and a , and all except the strongest spots on the zero layer-line must be re-examined, the second time with the cursor set at the reading $A' = \lambda K_\beta/a$. It is not safe to rely upon the detection of row-line coincidences by examination of layer-lines other than the zero layer-line.

TABLE I.

h, k indices of crystal planes which may produce spots on cubic or tetragonal (001) rotation photographs.

h	k	$h^2 + k^2$	$\sqrt{h^2 + k^2}$	h	k	$h^2 + k^2$	$\sqrt{h^2 + k^2}$
1	0	1	1·0	7	0	49	7·0
1	1	2	1·414	5	5	50	7·071
2	0	4	2·0	7	1		
2	1	5	2·236	6	4	52	7·211
2	2	8	2·828	7	2	53	7·280
3	0	9	3·0	7	3	58	7·616
3	1	10	3·162	6	5	61	7·810
3	2	13	3·606	8	0	64	8·0
4	0	16	4·0	7	4	65	8·06
4	1	17	4·123	8	1		
3	3	18	4·243	8	2	68	8·246
4	2	20	4·472	6	6	72	8·485
4	3	25	5·0	8	3	73	8·544
5	0			7	5	74	8·602
5	1	26	5·099	8	4	80	8·944
5	2	29	5·385	9	0	81	9·0
4	4	32	5·657	9	1	82	9·155
5	3	34	5·831	7	6	85	9·219
6	0	36	6·0	9	2		
6	1	37	6·083	8	5	89	9·434
6	2	40	6·325	9	3	90	9·487
5	4	41	6·403	9	4	97	9·849
6	3	45	6·708	7	7	98	9·899
				8	6	100	10·0

When, in the use of the instrument, the line of the cursor goes beyond the end of the graduations of the left-hand scale, the brass fitting is released and reclamped at the same A reading on the upper half of the middle scale, where it is used as before.

Partial Applications.

Fig. I can be very simply constructed by use of strips of semi-logarithmic paper pasted on cardboard. Instead of the rotating cursor of the instrument, a strip of glass or transparent xylonite having a black line ruled on it can then be used. Naturally this is not so convenient, as the reading on the middle scale has to be set each time.

The tables of constants given for the purpose of graduation of the right-hand scale of the instrument can be used for slide-rule calculation whenever reciprocal-lattice methods are to be used for interpretation of rotation photographs.

For example, in Table I. the constants of the middle column can be used to set the slide-rule cursor on the *top* scale of the slide-rule (when equation (2) is in use) or the constants in the third column can be set upon the *bottom* slide-rule scale.

Table II. gives the constants required for dealing with hexagonal or trigonal crystals. To get the equation (4) in suitable form for the present method, orthohexagonal axes are used, the crystals being referred to axes $a, b = a\sqrt{3}$, and c .

TABLE II.

Indices $(h k l)$, referred to orthohexagonal axes $a, b = a\sqrt{3}$ and c , of crystal planes which may produce spots on c -axis rotation photographs of trigonal or hexagonal crystals.

h	k	$h^2+k^2/3$.	$\{h^2+k^2/3\}^{1/2}$.	h	k	$h^2+k^2/3$.	$\{h^2+k^2/3\}^{1/2}$.
0	1	0.33	0.577	2	1	4.33	2.082
1	0	1.0	1.0	0	4	5.33	2.309
0	2	1.33	1.155	2	2		
1	2	2.33	1.527	1	4	6.33	2.516
0	3	3.0	1.732	2	3	7.0	2.646
2	0			0	5	8.33	2.887
1	3	4.0	2.0	3	0	9.0	3.0

h	k .	$h^2+k^2/3$.	$\{h^2+k^2/3\}^{1/2}$.	h	k .	$h^2+k^2/3$.	$\{h^2+k^2/3\}^{1/2}$.
1	5			6	1	36.33	6.027
2	4	9.33	3.055	5	6	37.0	6.083
3	1			2	10		
3	2	10.33	3.214	4	8	37.33	6.110
0	6	12.0	3.464	6	2		
3	3			6	3	39.0	6.245
2	5	12.33	3.511	0	11	40.33	6.351
1	6	13.0	3.606	1	11		
3	4	14.33	3.785	5	7	41.33	6.429
4	0	16.0	4.0	6	4		
2	6			3	10	42.33	6.506
0	7	16.33	4.031	4	9	43.0	6.557
4	1			6	5	44.33	6.658
1	7			2	11		
3	5	17.33	4.163	5	8	46.33	6.807
4	2			6	6		
4	3	19.33	4.397	0	12	48.0	6.928
2	7	20.33	4.509	7	0		
3	6	21.0	4.583	1	12	49.0	7.0
0	8	21.33	4.618	3	11		
4	4			4	10	49.33	7.024
1	8	22.33	4.726	7	1		
4	5	24.33	4.933	7	2	50.33	7.094
5	0	25.0	5.0	2	12		
2	8			5	9	52.0	7.211
3	7	25.33	5.033	7	3		
5	1			6	7	52.33	7.234
5	2	26.33	5.131	7	4	54.33	7.371
0	9	27.0	5.196	0	13		
1	9			4	11	56.33	7.505
4	6	28.0	5.292	3	12	57.0	7.550
5	3	28.33	5.322	1	13		
3	8	30.33	5.507	6	8	57.33	7.572
5	4			7	5		
2	9	31.0	5.568	5	10	58.33	7.637
4	7	32.33	5.686	2	13	60.33	7.767
0	10			7	6	61.0	7.810
5	5	33.33	5.773	6	9	63.0	7.937
1	10			8	0	64.0	8.0
6	0	34.0	5.859	4	12		
3	9			8	1	64.33	8.020

TABLE II. (cont.).

h	k .	$h^2+k^2/3$.	$\{h^2+k^2/3\}^{1/2}$.	h	k .	$h^2+k^2/3$.	$\{h^2+k^2/3\}^{1/2}$.
0 14				7 10		82.33	9.074
3 13				9 2			
5 11		65.33	8.082	3 15			
7 7				6 12		84.0	9.165
8 2				9 3			
1 14		66.33	8.144	0 16			
8 3		67.0	8.185	8 8		85.33	9.237
2 14				1 16			
6 10		69.33	8.326	9 4		86.33	9.291
8 4				2 16			
7 8		70.33	8.386	9 5		89.33	9.452
4 13				7 11			
8 5		72.33	8.504	5 14		90.33	9.504
5 12		73.0	8.544	4 15			
3 14				8 9		91.0	9.0
0 15		75.0	8.660	6 13		92.33	9.609
1 15				9 6		93.0	9.644
8 6				3 16		94.33	9.712
7 9		76.0	8.718	0 17		96.33	9.815
6 11		76.33	8.737	7 12		97.0	9.849
2 15		79.0	8.888	1 17			
8 7		80.33	8.963	9 7		97.33	9.866
9 0		81.0	9.0	8 10			
4 14				10 0		100.0	10.0
5 13		81.33	9.018	5 15			
9 1							

Table III. gives the constants for cubic [110] rotation photographs. Here it is better to have a different scale for each layer-line if the instrument is to be of general use. For economy in printing, only the square of the constant K is given. In graduating the scales the *square roots* of the numbers in the second column must be set off with the aid of a logarithmic ruler. It should be remembered that for a *face-centred* lattice (F or $\Gamma r'$) X-ray reflexions can occur only from planes whose indices are all odd or all even (0 is even). That is, planes having mixed indices cannot produce spots on the rotation photograph. For the *body-centred* lattice (B or $\Gamma r''$) reflexions can occur only from those planes the sum of whose indices is an even number. It is therefore unnecessary to determine the theoretical

TABLE III.

Indices ($h k l$) of crystal planes which may produce spots upon cubic [110] rotation photographs.

Zero Layer-line. $h+k=0$.

h	k	l	K.	Lattice.	h	k	l	K.	Lattice.
0	0	1	1		5	5	0	50	B
1	1	0	2	B	5	5	1	51	F
0	1	1	3	F	1	1	7		
0	0	2	4	B F	5	5	2		
1	1	2	6	B	3	3	6	54	B
2	2	0	8	B F	4	4	5	57	
2	2	1	9		2	2	7		
0	0	3			5	5	3	59	F
1	1	3	11	F	0	0	8	64	B F
2	2	2	12	B F	5	5	4	66	B
0	0	4	16	B F	1	1	8		
2	2	3	17		3	3	7	67	F
3	3	0	18	B	4	4	6	68	F
1	1	4			6	6	0	72	B F
3	3	1	19	F	2	2	8		
3	3	2	22	B	6	6	1	73	
2	2	4	24	B F	5	5	5	75	F
0	0	5	25		6	6	2	76	B F
3	3	3	27	F	0	0	9		
1	1	5			4	4	7	81	
4	4	0	32	B F	6	6	3		
4	4	1	33		3	3	8	82	B
2	2	5			1	1	9	83	F
3	3	4	34	B	5	5	6	86	B
0	0	6	36	B F	6	6	4	88	B F
4	4	2			2	2	9	89	
1	1	6	38	B	4	4	8	96	B F
4	4	3	41		6	6	5	97	
3	3	5	43	F	7	7	0	98	B
2	2	6	44	F	7	7	1		
4	4	4	48	B F	5	5	7	99	
0	0	7	49		3	3	9		
					0	0	10	100	B F

TABLE III. (cont.).

First Layer-line. $h+k=1$. Absent for F.

h	k	l	K.	Lattice.	h	k	l	K.	Lattice.
1	0	0	0·5		2	1	7	53·5	B
1	0	1	1·5	B	5	4	4	56·5	
1	0	2	4·5		6	5	0		
2	1	1	5·5	B	4	3	6	60·5	
2	1	2	8·5		3	2	7		
1	0	3	9·5	B	6	5	1	61·5	B
3	2	0	12·5		1	0	8		
3	2	1	13·5	B	6	5	2	64·5	
1	0	4			5	4	5	65·5	B
3	2	2	16·5		2	1	8	68·5	
2	1	4	20·5		6	5	3	69·5	B
3	2	3	21·5	B	4	3	7	73·5	B
4	3	0	24·5		6	5	4		
1	0	5	25·5	B	3	2	8	76·5	
4	3	1	25·5		1	0	9	81·5	B
4	3	2	28·5		7	6	0	84·5	
2	1	5	29·5	B	6	5	5		
4	3	3	33·5	B	7	6	1		
1	0	6	36·5		2	1	9	85·5	B
3	2	5	37·5	B	7	6	2		
2	1	6			4	3	8	88·5	
4	3	4	40·5		5	4	7	89·5	B
5	4	0			3	2	9		
5	4	1	41·5	B	7	6	3	93·5	B
5	4	2	44·5		6	5	6	96·5	
3	2	6	48·5						
1	0	7							
4	3	5	49·5	B					

Second Layer-line. $h+k=2$.

h	k	l	K.	Lattice.	h	k	l	K.	Lattice.
1	1	1	1	F	2	0	3	11	
2	0	0	2	B F	3	1	2	12	B
2	0	1	3		1	1	4	16	B
1	1	2	4	B	3	1	3	17	F
2	0	2	6	B F	4	2	0	18	B F
3	1	0	8	B	4	2	1	19	
3	1	1	9	F	4	2	2	22	B F

TABLE III. (cont.).

Second Layer-line. $h+k=2$. (Cont.)

h	k	l	K.	Lattice.	h	k	l	K.	Lattice.
3	1	4	24	B	2	0	8	66	B F
1	1	5	25	F	6	4	4		
2	0	5	27		4	2	7	67	
4	2	3			5	3	6	68	B
5	3	0	32	B	3	1	8	72	B
5	3	1	33	F	7	5	0		
4	2	4	34	B F	7	5	1	73	
1	1	6	36	B	6	4	5	75	
5	3	2			7	5	2	76	B
2	0	6	38	B F	7	5	3		
5	3	3	41	F	1	1	9	81	
4	2	5	43		4	2	8	82	B F
3	1	6	44	B	2	0	9	83	
5	3	4	48	B	6	4	6	86	B F
1	1	7	49	F	7	5	4	88	B
6	4	0	50	B F	3	1	9	89	
2	0	7	51		5	3	8	96	B
6	4	1			7	5	5	97	
6	4	2	54	B F	8	6	0	98	B F
3	1	7	57		4	2	9		
5	3	5			6	4	7	99	
6	4	3	59		8	6	1		
1	1	8	64	B					

Third Layer-line. $h+k=3$. Absent for F.

h	k	l	K.	Lattice.	h	k	l	K.	Lattice.
2	1	0	0·5	B	3	0	5	29·5	B
2	1	1	1·5	B	5	2	3	33·5	B
2	1	2	4·5		2	1	6	36·5	
3	0	0			4	1	6	37·5	B
3	0	1	5·5	B	6	3	0	40·5	
3	0	2	8·5		5	2	4		
2	1	3	9·5	B	6	3	1	41·5	B
4	1	0	12·5		6	3	2	44·5	
3	0	3	13·5		4	1	6	48·5	
4	1	1			2	1	7		
4	1	2	16·5		5	2	5	49·5	B
3	0	4	20·5		6	3	3		
4	1	3	21·5	B	3	0	7	53·5	B
5	2	0	24·5		6	3	4	56·5	
5	2	1	25·5	B	5	2	6	60·5	
4	1	4	28·5		7	4	0		
5	2	2							

TABLE III. (cont.)

Third Layer-line. $h+k=3$. Absent for F. (Cont.)

h	k	l	K.	Lattice.	h	k	l	K.	Lattice.
7	4	1	61·5	B	2	1	9	81·5	B
2	1	8	64·5		8	5	0	84·5	
7	4	2			3	0	9		
6	3	5	65·5	B	7	4	5	85·5	B
3	0	8	68·5		8	5	1		
7	4	3	69·5	B	8	5	2	88·5	
5	2	7	73·5	B	6	3	7	89·5	B
4	1	8			4	1	9	93·5	B
6	3	6	76·5		8	5	3		
7	4	4			7	4	6	96·5	

Fourth Layer-line. $h+k=4$.

h	k	l	K.	Lattice.	h	k	l	K.	Lattice.
2	2	1	1		7	3	0	50	B
3	1	0	2	B	7	3	1	51	F
3	1	1	3	F	5	1	6		
2	2	2	4	B	7	3	2	54	B
3	1	2	6	B	4	0	7		
4	0	0	8	B F	6	2	5	57	
2	2	3			7	3	3	59	F
4	0	1	9		2	2	8	64	B F
3	1	3	11	F	3	1	8	66	B
4	0	2	12	B F	7	3	4		
2	2	4	16	B F	5	1	7	67	F
4	0	3	17		6	2	6	68	B F
3	1	4			8	4	0	72	B F
5	1	0	18	B	8	4	1	73	
5	1	1	19	F	7	3	5	75	F
5	1	2	22	B	8	4	2	76	B F
4	0	4	24	B F	6	2	7		
2	2	5	25		8	4	3	81	
5	1	3	27	F	2	2	9		
6	2	0	32	B F	5	1	8	82	B
4	0	5			3	1	9	83	
6	2	1	33		7	3	6	86	B
5	1	4	34	B	8	4	4	88	B F
6	2	2	36	B F	4	0	9	89	
3	1	6	38	B	6	2	8	96	B F
6	2	3	41		8	4	5	97	
5	1	5	43	F	9	5	0	98	B
4	0	6	44	B F	7	3	7		
6	2	4	48	B F	9	5	1	99	F
2	2	7	49						

values of ξ and ζ for such planes, as the lattice of a particular crystal can always be readily determined. Accordingly, in the third column of the table, the lattice is indicated. Reflexions may be observed from any of the planes if the lattice is simple cubic ($I\bar{r}$). In preparing the scales, the planes marked B may be indicated with a half graduation to the right, those marked F with half graduation to the left, the others with a full graduation right across the vertical line. This table should be of use, especially in metallurgical work. It will be noted that there is much less likelihood of spots being unresolvable in this type of rotation photograph than for the simple c -axis rotation (cf. Table I.).

In conclusion, it may be added that in actual practice the method here described, used in conjunction with that given in Part I., is so rapid that the film can be interpreted whilst it is undergoing fixation in the hypo-bath. It will, of course, be understood that unresolvable spots (especially those having high indices, hkl) may occur, but they are then unresolvable by any method of interpretation. It is then necessary to resort to oscillation or moving film or ionization spectrometer methods, which give additional information as to the position of the crystal when it is producing a particular reflexion. In Part III. it is hoped to deal with an instrument applicable to such cases.

The present instrument was made, with the help of a Royal Society Government Grant, in the workshops of the Physics Department of the University of Leeds by Mr. Ludbrook, to whom some of the details are due.

References.

- (1) George, Phil. Mag. vii. pp. 373-384 (1929).
- (2) Wyckoff, 'Structure of Crystals,' pp. 97-99 (1924).
- (3) Schiebold, *Zs. f. Phys.* xxviii. pp. 355-370 (1924).
- (4) Ewald, *Zs. f. Krist.* lvi. pp. 129-156 (1921).
- (5) References are given in *Zs. f. Phys.* xxiii. pp. 337-340 (1924).
- (6) *Bull. Soc. Française de Min.* xlvi. pp. 5-32 (1926).
- (7) Roy. Soc. Proc. A, cxiii. pp. 117-160 (1926).
- (8) Polanyi and Weissenberg, *Zs. f. Phys.* x. p. 49 (1922).
- (9) For example, D'Ocagne, 'Traité de Nomographie,' Paris, 1899, or Brodetsky, 'Nomography,' London, 1920.

XLIX. The Effects of Magnetic Field on certain Chemical Reactions. By S. S. BHATNAGAR, D.Sc.(Lond.), F.Inst.P., R. N. MATHUR, M.Sc., and R. N. KAPUR, M.Sc.*

THE close relationship between electricity and chemical affinity on the one hand and that between electricity and magnetism on the other early raised the question whether magnetism would alter the character or degree of a chemical reaction. As early as 1881 Ramsen † observed that magnetism had a remarkable action on the deposition of copper from solution of its salts on an iron plate. In 1886 Nichols ‡ further investigated the action of acids on iron in a magnetic field, and in 1887 H. A. Rowland and Louis Bell read a paper at the Manchester Meeting of the British Association, September 1887, on "An Explanation of the Action of a Magnet on Chemical Action." They explained the protection of iron from the chemical action of hydrochloric acid in lines around the edge of the poles on the view that the force acting on the particle in any direction is proportional to the rate of variation of the square of the magnetic force in that direction. "This rate of variation is greatest near the edges and points of a magnetic pole, and more work will be required to tear away a particle of iron and steel from such an edge or point than from a hollow. This follows whether the tearing away is done mechanically or chemically."

Loeb § in 1891 and later Wolff || tried the influence of magnetic field on the oxidation and reduction of iron salts, but obtained negative results. Jahr ¶ observed that a photographic plate immersed in a developer or even in distilled water is affected when brought near the pole of an electromagnet consisting of a bundle of steel wires.

Alexander De Hemptenine ** in 1900 published an interesting paper in which he showed that although theoretically there is an effect of the magnetic field, experimentally it is too small to be of much consequence. Among

* Communicated by the Authors.

† Ramsen, Amer. Chem. Journ. iii. p. 157 (1881).

‡ Nichols, Amer. Journ. Science, p. 372 (1886).

§ Loeb, Amer. Chem. Journ. xiii. pp. 145-53 (1891).

|| F. A. Wolff, Amer. Chem. Journ. xvii. pp. 122-138 (1895).

¶ E. Jahr, *Electro-Chem. Zeitschr.* v. pp. 177-180 (1898).

** Alexander De Hemptenine, *Zeit. Physikal. Chem.* xxxiv. p. 669 (1900).

the later workers Berndt * found that the rate of solution of iron in hydrochloric acid in a magnetic field is smaller. With zinc no difference was observed. Recently Schukarew † performed a series of experiments to detect any possible effect on a number of chemical reactions by subjecting them to transverse and longitudinal magnetic fields ranging from 2000 to 7000 gauss. No general conclusions could be reached by him. According to Parker and Armes ‡ the reduction of ferric chloride by iron and aluminium and the reduction of permanganate in acid solutions by metallic iron are accelerated by the field. Henglein §, however, found no difference in the combination of NO and Cl even with fields up to 20,000 gauss.

THEORETICAL.

For ferromagnetic bodies the reasons advanced by Rowland to explain the action of magnetic field on the dissolution of iron in hydrochloric acid and De Hemptenine's treatment of the subject on thermodynamic basis are worthy of mention. Taking, however, the more general case of para- and diamagnetic substances there are a number of theoretical reasons to expect an influence of an impressed magnetic field on chemical reactions.

Magnetism has been shown to have a profound influence on valence. G. N. Lewis || has discussed at length the magneto-chemical theory of valence. A chemical bond according to him is the pairing of two electrons and two isolated electronic orbits or magnets tend to couple with one another to eliminate their magnetic moment. E. H. Williams ¶ has emphasized the scarcity of odd molecules, i.e. molecules having an odd number of electrons among the chemical compounds.

If, then, a chemical reaction involves change in valence of the reacting substances an external magnetic field must necessarily affect the reaction. Even in the case of double decomposition in which there is no actual change in the valence there may be a change in the magnetic moments of

* G. Berndt, *Physikal. Zeitschr.* ix. p. 512 (1908).

† A. Schukarew, *Zeit. Physikal. Chem.* cxiii. p. 441 (1924).

‡ M. A. Parker and H. P. Armes, *Trans. Roy. Soc. Canada*, xviii. III, p. 203 (1924).

§ F. A. Henglein, *Zeit. Electro-Chem.* xxxii. p. 213 (1926).

|| G. N. Lewis, "Valence and Structure of Atoms and Molecules," Amer. Chem. Soc., Monographs (1923); also "The Magneto-Chemical Theory in Chemical Reviews," vol. i. no. 2 (1924).

¶ E. H. Williams, *Phys. Rev.* xxviii. p. 167 (1926).

the initial and final products. If during a reaction the magnetic moments tend to decrease then the presence of an external field will try to "conserve" the magnetism and so retard the rate of reaction. On the other hand, if the magnetic moment increases during the course of reaction, then the presence of a field will further help the increase and so accelerate the rate of reaction.

The idea is essentially of a system possessing inertia and by analogy may be called the "magnetic inertia" of the system.

We may consider the above in the light of the law of mass action. If A and B denote the concentrations of two reacting substances and C and D the concentrations of the reaction products, then for the equilibrium state we have

$$A \times B \times K_1 = C + D \times K_2$$

$$\text{or } \frac{A \times B}{C \times D} = \frac{K_2}{K_1} = K$$

where K_1 , K_2 , and K are the usual constants. For any given concentration the velocities of the forward and backward reactions will then depend upon the constants K_1 and K_2 . These constants while independent of concentrations may vary with the temperature, the nature of the medium, and other physical conditions.

On the basis of the kinetic theory a molecule (or an ion) A, when it collides with B, either unites with it to form a third substance C or rebounds elastically. The rate of formation of C will then depend upon the number of inelastic collisions per second between A and B. Any agency, whether internal or external, which affects the probability of inelastic conditions also affects the rate of reaction A + B. In a magnetic field the atoms (and presumably ions also) become spatially quantized, that is to say, they tend to assume certain definite positions relative to one another. And thus the collisions within the field are likely to take place in a more orderly and directed manner and the probability of inelastic collisions should change, and with it the velocity of the reaction also.

Thus, we conclude that a chemical transformation from diamagnetic to paramagnetic or less diamagnetic state should be accelerated, and that from a paramagnetic to diamagnetic or from a feebly diamagnetic to more strongly diamagnetic state should be retarded.

Considering again the above reacting system, it is evident

that if one of the reaction products possesses a different magnetic state from the rest, it would tend to localize itself in certain parts of the field and to withdraw itself from other parts. The reaction velocity A+B will then also vary accordingly. Following similar considerations Weigle* has obtained a mathematical relation between the concentrations inside and outside the magnetic field. This will be more fully discussed later.

EXPERIMENTAL.

A critical study of the previous work on the subject shows that in almost all cases where negative results were obtained, the reasons might be ascribed to the one or the other of the following causes :—

1. The reactions used proceeded with great velocity, *e.g.*, the oxidation of ferrous salts.
2. The analytical methods employed were incapable of measuring small changes in the amounts of reaction products.
3. There was no appreciable difference between the susceptibilities of the initial and the final reaction products.

Care was therefore taken in this investigation to select reactions with very small reaction velocity. Also reactions involving large changes in the susceptibilities of initial and final products were selected. The titration methods of analysis employed were found quite adequate.

The reactions were conducted in ordinary test-tubes which could be clamped within the pole-pieces of an electromagnet. In each case a control experiment was conducted side by side under identical conditions and temperatures were recorded. There was no appreciable temperature difference between the control and the reaction within the field. In order to be certain of any influence of the material of the test-tubes themselves on the reactions, the control and reaction tubes were interchanged each time. No difference due to tubes only was, however, detected. Only Merck's extra pure chemicals and reagents were used throughout.

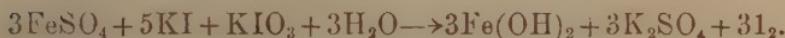
A fairly large electromagnet provided the field. The strength varied from 600 to 1700 gauss with a gap of 1 cm. between the pole-pieces, which were conical and had a plane face of about 1 cm. diameter. A micrometric arrangement for adjustment of distance was provided. The current

* J. J. Weigle, Phys. Rev. xxxi. pp. 676-9 (1928).

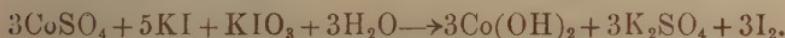
passing through the electromagnet was kept constant by a variable rheostat and an ammeter.

The following reactions have been studied :—

1. Reduction of ferric chloride solution containing hydrochloric acid by metallic iron, aluminium, and zinc.
2. Dissolution of the metals iron, aluminium, and zinc in dilute hydrochloric acid.
3. The oxidation of oxalic acid by potassium permanganate.
4. Reduction of chromic acid by phosphorous acid.
5. Oxidation of potassium iodide by chromic acid.
6. Reduction of potassium permanganate by chloral hydrate.
7. The reaction :—



8. The Reaction :—



9. Oxidation of hydriodic acid by hydrogen peroxide.

10. Esterification of acetic acid by hydrogen chloride.

We may now consider each of the reactions separately.

1. *Reduction of Ferric Chloride Solution containing Hydrochloric Acid by Metallic Iron, Aluminium, and Zinc.*—The velocity of reduction was measured by adding a weighed quantity of the metal to a known definite volume of the ferric chloride solution. After the reaction had proceeded for some time, a small quantity was pipetted out and titrated against a standard solution of potassium bichromate. From this the amount of Fe reduced was calculated.

The reaction mixture was stirred equally at intervals of 5 minutes during the course of reduction. It has been noted that stirring has a considerable influence on the rate of the reaction.

The reduction of ferric chloride in cases (1) and (3) in Table I. (p. 462) was also tried under different field strengths by varying the current in the electromagnet. The results obtained were similar to the above, and showed with iron a progressive increase and with zinc a progressive decrease in the velocity with increasing field strength.

The rate of reduction of ferric chloride solution is thus accelerated by iron and aluminium in magnetic field, while with zinc it is retarded.

TABLE I.

Strength of FeCl_3 solution = 162.50 gms. per litre.

Weight of the metal taken = 1.00 gm.

Temperature = 15.0° C.

Field strength = 1700 gauss.

Reaction.	Interval.	Titre value with N/50 potassium dichromate.		Change due to magnetic field calculated as amount of iron.	Remarks.
		Without field.	Within field.		
1. Ferric chloride and iron filings.	1/2 hr.	11.00	12.50	0.0017 gm.	Reaction
	1 hr.	19.00	21.50	0.0028 „	accelerated
	1½ hr.	30.50	34.50	0.0045 „	by field.
	2 hrs.	45.00	50.00	0.0056 „	
2. Ferric chloride and aluminium.	1/2 hr.	8.50	9.00	0.0006 „	Reaction
	1 hr.	29.00	30.50	0.0017 „	accelerated
	1½ hrs.	38.25	40.00	0.0020 „	by field.
	2 hrs.	47.00	49.00	0.0022 „	
3. Ferric chloride and zinc.	1/2 hr.	4.30	3.00	0.0014 „	Reaction
	1 hr.	14.60	12.80	0.0021 „	retarded
	1½ hrs.	30.40	27.50	0.0032 „	by field.
	2 hrs.	47.10	43.00	0.0046 „	

2. *The Dissolution of Metals in Dilute Hydrochloric Acid.*—According to Conroy *, who worked with iron, and Auren †, who used zinc, the reaction takes place in two periods. During the initial or "induction period" the reaction is slow. It then increases to a maximum and then finally falls down.

The rate of dissolution was determined in the following way :—

A definite volume of dilute hydrochloric acid was added to a known weight of metal cut into small pieces. After a definite time a small volume of reaction mixture was taken out and titrated for the amount of acid left against a standard solution of sodium hydroxide.

* James T. Conroy, *J. Soc. Chem. Ind.* **xx**. p. 316 (1901).

† T. Ericson Auren, *Zeits. anorg. Chem.* **xxvii**. p. 209 (1901).

The results are recorded below :

TABLE II.

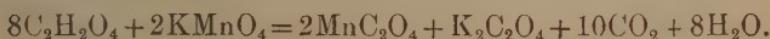
Temperature = 16° C.

Field strength = 1700 gauss.

Reaction.	Interval.	Titre value with N/100 sodium hydroxide.		Change due to magnetic field.	Remarks.
		Without field.	Within field.		
Iron in HCl (1·7N)	1/2 hr.	336·00	337·00	1·00	Rate of dissolution re-
1 gm. Fe in 10 c.c. acid.	1 „	334·00	335·00	1·00	tarded by field.
Zinc in HCl (1·15N)	1/2 „	330·00	333·00	3·00	
2 gm. Zn. in 10 c.c. acid.	1 ½ „	326·00	331·00	5·00	
Zinc in HCl (1·15N)	2 „	229·00	227·50	1·50	Rate of dissolution ac-
Aluminium in HCl (·78N)	1/2 hr.	227·00	225·50	1·50	celerated by field.
1·5 gm. Al. in 10 c.c. acid.	1 ½ „	225·00	223·00	2·00	
Aluminium in HCl (·78N)	2 „	222·50	220·00	2·50	
Aluminium in HCl (·78N)	1/2 hr.	155·00	155·00	No difference.	No appreciable difference.
1 gm. Al. in 10 c.c. acid.	1 „	154·00	154·00	„	
1·5 gm. Al. in 10 c.c. acid.	1 ½ „	153·00	153·00	„	
Aluminium in HCl (·78N)	2 „	151·50	151·00	0·50	

The results shown above indicate that the rate of the dissolution of iron in dilute hydrochloric acid is slightly retarded by the magnetic field, while that of zinc is slightly accelerated. In the case of aluminium no appreciable difference is observed.

3. *The Oxidation of Oxalic Acid by Potassium Permanganate.*—According to Richard Ehrenfeld *, the reaction takes place quantitatively between potassium permanganate and oxalic acid in absence of mineral acids, according to the equation :



The velocity of the reaction was measured by mixing the substances in solution both (a) outside magnetic field and (b) inside the magnetic field, and after a definite time a

* Richard Ehrenfeld, *Zeit. anorg. Chemie*, xxxiii. p. 117 (1902).

certain amount was taken out of the reaction mixture and added to a mixture of dilute sulphuric acid and potassium iodide. The liberated iodine was then estimated by titration against sodium thiosulphate. From the amount of iodine the amount of permanganate which had been decomposed was calculated.

TABLE III.

Strength of the potassium permanganate solution =

1.05 gms. per litre.

Strength of the oxalic acid solution = 6.0 gms. per litre.

Temperature = 17.5° C.

Field strength = 1700 gauss.

Interval.	Titre value with N/50 sodium thiosulphate.		Change due to magnetic field calculated as the amount of KMnO_4 decomposed.	Remarks.
	Without field.	Within field.		
1/2 hr. ...	3.10 c.c.	2.85 c.c.	0.00016 gm.	The rate of oxidation is accelerated by the magnetic field.
3/4 , , ...	2.40 , ,	2.05 , ,	0.00022 , ,	
1 " , , ...	1.70 , ,	1.20 , ,	0.00032 , ,	

It is clear from the results tabulated above that the rate of oxidation of oxalic acid by potassium permanganate is accelerated by the magnetic field. Further experiments showed that the difference in KMnO_4 decomposed within and without the magnetic field changes with the strength of the field.

4. *The Reduction of Chromic Acid by Phosphorous Acid.*—This was studied by Viard*. The velocity of the reduction was determined by mixing the two substances in solution, and after a definite time taking out a certain volume of the reaction mixture and adding to it dilute sulphuric acid and potassium iodide. The liberated iodine was estimated, and from it the amount of chromic acid which had been reduced was calculated.

Several test experiments had to be performed to find out whether the presence of phosphorous acid creates any difficulty in the accurate determination of chromic acid. No trouble, however, occurs due to this.

* G. Viard, *Comp. Rend.* cxxiv. p. 148 (1897).

TABLE IV.

Strength of the chromic acid solution = 49·6 gms. per litre.
 Strength of phosphorous acid solution = 60 per cent.

Temperature = 24·0° C.
 Field strength = 1700 gauss.

Interval.	Titre value with N/10 sodium thiosulphate.		Change due to magnetic field calculated as the amount of chromic acid reduced.	Remarks.
	Without field.	Within field.		
1/2 hr.	5·20 c.c.	4·45 c.c.	0·0029 gm.	The reduction
3/4 ,.	4·20 ,.	3·40 ,.	0·0031 ,.	is accelerated
1 "	3·70 ,.	2·80 ,.	0·0035 ,.	by the
1½ "	2·80 ,.	1·60 ,.	0·0047 ,.	field.

The above table shows that the rate of reduction of chromic acid by phosphorous acid is accelerated in magnetic field. Also, further experiments showed that the difference in reduction within and without the field decreases as the strength of the magnetic field is decreased.

5. *The Oxidation of Potassium Iodide by Chromic Acid.*—Delury *, who studied this reaction, found that the rate of the liberation of iodine is approximately proportional to the square of the concentration of the acid.

The rate of the reaction was measured by mixing the two substances in solution, and after some time putting the whole reaction mixture in a large volume of ice-cold water and titrating the iodine liberated. The results are recorded in the table below :—

TABLE V.

Strength of the potassium iodide solution = 40 gms. per litre.
 Strength of the chromic acid solution = 12·87 gms. per litre.

Temperature = 25° C.
 Field strength = 1700 gauss.

Interval.	Titre value with N/10 sodium thiosulphate.		Change due to field calculated as the weight of iodine liberated.	Remarks.
	Without field.	Within field.		
1 hr.	11·05 c.c.	11·60 c.c.	0·00007 gm.	The liberation of iodine is accelerated
2 ,.	11·90 ,.	12·70 ,.	0·00010 ,.	by the field.

* R. E. Delury, J. Phys. Chem. vii. p. 239 (1903).

The results given in Table V. (p. 465) show that the rate of the liberation of iodine by the action of the chromic acid on potassium iodide is accelerated to some extent. Also it was found that the difference in the amount of iodine liberated within and without magnetic field falls with decreasing strength of the magnetic field.

6. *The Reduction of Potassium Permanganate by Chloral Hydrate.*—It has been proved by Aladar Buzagh* that the reaction between potassium permanganate and chloral hydrate takes place quantitatively.

The velocity of the reaction was measured by the following method :—

A known volume of chloral hydrate (of known strength) was added to a measured volume of potassium permanganate. After a known interval of time the whole of the reaction mixture was added to dilute sulphuric acid and potassium iodide, and as before the liberated iodine was titrated.

TABLE VI.

Strength of potassium permanganate solution = 3·15 gms.
per litre.
Strength of the chloral hydrate solution = 250 gms. per litre.
Temperature = 25·0° C.
Field strength = 1700 gauss.

Interval.	Titre value with N/100 sodium thiosulphate.		Change due to magnetic field calculated as the amount of KMnO_4 reduced.	Remarks.
	Without field.	Within field.		
10 mts.	18·70 c.c.	18·30 c.c.	0·00013 gm.	The reduction is accelerated by the magnetic field.
45 „	15·50 „	14·60 „	0·00028 „	
2 hrs.	10·50 „	8·30 „	0·00070 „	

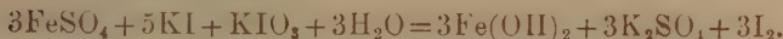
From the above results it appears that there is acceleration in the rate of the reduction of potassium permanganate by chloral hydrate in the magnetic field. Also it was found that the rate of reduction changes with the strength of the magnetic field.

In the reactions from Nos. 7 to 10, the magnetic field does not produce any difference in the velocity of reaction. The largest difference observed is 0·30 c.c. after

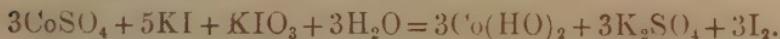
* Aladar Buzagh, *Matematikai es Termeszettudomanyi Ertesito* xl. p. 134 (1923).

an interval of $1\frac{1}{2}$ hours, and this could be well within experimental error. The methods of estimation and some results are given below:—

7. The Reaction :



8. The Reaction :



The velocities were determined by estimating the iodine liberated as in the reaction 5.

TABLE VII.

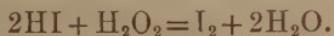
Field strength=1300 gauss

Temperature=21°.

Field strength=1700 gauss.

Reaction.	Interval.	Titre value with N/100 sodium thiosulphate.		Change due to magnetic field.	Remarks.
		Without field.	Within field.		
7.	1/2 hr.	5.10 c.c.	5.10 c.c.	0.00 c.c.	No appreciable difference.
	1 " "	6.55 "	6.80 "	0.25 "	No appreciable difference.
	1½ "	7.55 "	7.85 "	0.30 "	
8.	1/4 hr.	5.70 "	5.75 "	0.05 "	No appreciable difference.
	1/2 "	6.70 "	6.80 "	0.10 "	
	1 "	7.40 "	7.50 "	0.10 "	
	1½ "	7.90 "	7.90 "	0.00 "	

9. *Oxidation of Hydriodic Acid by Hydrogen Peroxide.*—According to Noyes and Scott *, the oxidation takes place quantitatively according to the equation :



The liberated iodine was titrated as in the last reaction.

10. *The Esterification of Acetic Acid by Alcoholic Hydrogen Chloride.*—The course of the reaction was followed by mixing the two solutions, and after a definite time titrating against standard barium hydroxide solution, using phenolphthalein as an indicator.

* Arthur A. Noyes and Walter O. Scott, *Zeit. Phys. Chem.* xviii. p. 118 (1895).

We can now summarize the results obtained so far as below:—

Reaction 1. Reduction of ferric chloride solution containing hydrochloric acid;

- (a) with iron . . . is accelerated by magnetic field.
- (b) with aluminium is accelerated by magnetic field.
- (c) with zinc . . . is retarded by magnetic field.

Reaction 2. Dissolution of metals in dilute hydrochloric acid;

- (a) the dissolution of zinc is accelerated by magnetic field.
- (b) the dissolution of iron is retarded by magnetic field.
- (c) the dissolution of aluminium is not influenced by magnetic field.

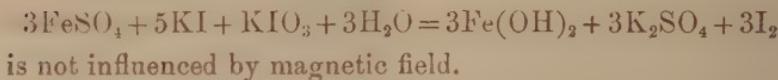
Reaction 3. The oxidation of oxalic acid by potassium permanganate is accelerated by magnetic field.

Reaction 4. Reduction of chromic acid by phosphorous acid is accelerated by magnetic field.

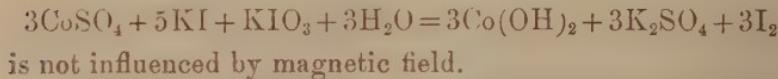
Reaction 5. Oxidation of potassium iodide by chromic acid is accelerated by magnetic field.

Reaction 6. Reduction of potassium permanganate by chloral hydrate is accelerated by magnetic field.

Reaction 7. The reaction



Reaction 8. The reaction



Reaction 9. Oxidation of hydriodic acid by hydrogen peroxide is not influenced by magnetic field.

Reaction 10. Esterification of acetic acid by alcoholic hydrogen chloride is not influenced by magnetic field.

A close study of the above with the magnetic properties of the reacting molecules enables us to draw some general conclusions. It is evident that the velocity of the reaction is increased in those homogeneous reactions in which the sum of the molecular susceptibilities of the reactants becomes greater as the reaction proceeds.

In Table VIII. we have put together the homogeneous reactions tried by us. Below each of the reactants we have given its molecular susceptibility. In column 2, $\Sigma \chi_{M_i}$ gives the sum of the molecular susceptibilities of the initial substances of the reaction, while in column 3, $\Sigma \chi_{M_f}$ gives the sum for the final products. We have here left out of consideration the case of heterogeneous reactions. The presence

TABLE VIII.

Reaction.	$\Sigma \chi M_i$.	$\Sigma \chi M_f$.	Change in reaction.
3. $2\text{KMnO}_4 + 8\text{C}_2\text{H}_2\text{O}_4 = 2\text{MnC}_2\text{O}_4 + \text{K}_2\text{C}_2\text{O}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O}$	149.6	44624.96	Acceleration.
$632.0 + (-482.4) \rightarrow 44787.6$			
$+(-68.06) + (+7.48) + (102.08)$			
4. $2\text{CrO}_3 + 2\text{H}_2\text{O} + 3\text{H}_3\text{PO}_4 = \text{Cr}_2\text{O}_3 + 2\text{H}_2\text{O} + 3\text{H}_3\text{PO}_4$	-47.72	3774.48	Acceleration.
$150 + (-25.52) + (-172.2) \rightarrow 3800$			
$+(-25.52)$			
5. $2\text{CrO}_3 + 2\text{H}_2\text{O} + \text{H}_2\text{O} + 6\text{KI} = \text{Cr}_2\text{O}_3 + 3\text{I}_2 + 6\text{KOH}$	-336.48	3499.7	Acceleration.
$150 + (-25.52) + (-12.76)$			
$+(448.2) \rightarrow 3800 + (-182.7)$			
$+(-117.6)$			
6. $2\text{KMnO}_4 + 3\text{CCl}_3\text{CH}(\text{OH})_2 = 2\text{MnO}_2 + 2\text{KOH} + 3\text{CCl}_3\text{COOH}$	329.48	4658.8	Acceleration.
$632.0 + (-302.86) \rightarrow 4698$			
$+(-39.2)$			
9. $2\text{HI} + \text{H}_2\text{O}_2 = \text{I}_2 + 2\text{H}_2\text{O}$	-111.66	-114.42	No appreciable effects.
$(-79.36) + (-32.30) \rightarrow (-83.90)$			
$+(-25.52)$			
10. $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH} = \text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O}$	-65.08	-65.1	No appreciable effects.
$(-41.4) + (-23.68) \rightarrow (52.54)$			
$+(-12.76)$			

NOTE. In reaction 4 the value of H_3PO_4 is neglected. As it is diamagnetic its value will necessarily be very small and not likely to affect the result in the presence of the strongly paramagnetic substances. Similarly for CCl_3COOH in reaction 5.

of the solid phase in such reactions is a great disturbing factor. Moreover, the kinetics of some of these reactions are not clearly understood. The values of the molecular susceptibilities given in the above table are taken from Landolt and Börnstein's 'Physikalisch-Chemische Tabellen.' A few of the values not given in the tables had to be experimentally determined in the laboratory on a magnetic balance of the Wilson type, as set up in this laboratory for work on electronic isomers*.

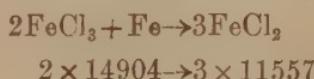
It will be noticed that most of the values of the molecular susceptibilities given in the table refer to those of the

* S. S. Bhatnagar and C. L. Dhawan, Phil. Mag. v. p. 536 (1928); S. S. Bhatnagar and R. N. Mathur, Phil. Mag. vi. p. 217 (1928).

substances in the crystalline form and not in solution, which is the form in which the substances exist in the case of the chemical reactions. Epstein * and Gerlach † have shown that the susceptibility of the paramagnetic salts is independent of their being in solution or in the solid state, and that ions, whether in solution or in a space lattice, are arranged relatively to an external magnetic field in accordance with the quantum theory. Also from a study of the values of ionic moments given by Stoner ‡, it is evident that even experimentally determined values do not differ materially from the values deduced from the salts in the solid state.

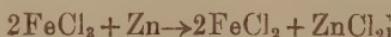
In the reactions given in Table VIII, Nos. 3, 4, 5, and 6 are those in which the sum of the molecular susceptibilities of the final products is very much larger than that of the initial resultants. In the reactions 9 and 10 the summation values in the two cases are almost the same, and the very small change in the velocities within and without the magnetic field is obviously too small to show any detectable change in the velocity.

With heterogeneous reactions numerical evaluation is much complicated by the very incomplete knowledge we possess of the exact mechanism. In reaction 1 (a), for example, the molecular susceptibility of FeCl_3 is 14904×10^{-6} (taking mass susceptibility of $\text{FeCl}_3 = 91 \times 10^{-6}$ from Townsend's data), and that of $\text{FeCl}_2 = 11557 \times 10^{-6}$. In 1 (a) where iron is used for reduction the equation can be expressed as



as iron is used in metallic form, its ionic moment would be zero (or at any rate very small), and so the final product has a greater total susceptibility than the initial. The reaction is accordingly accelerated inside the magnetic field.

In the reaction 1 (c) where zinc is used, the final equation most probably is



as zinc chloride is diamagnetic, the total of the molecular susceptibilities of the final products is less than the initial,

* Epstein, 'Science,' lvii. p. 532 (1923).

† Gerlach, *Phys. Zeits.* xxiv. p. 275 (1923).

‡ Stoner, 'Magnetism and Atomic Structure,' pp. 127-136.

and we find here a retardation in the velocity with the field.

We can now express the results obtained symbolically thus, when

$$\Sigma \chi_{Mf} > \Sigma \chi_{Mi} \text{ the rate of reaction is accelerated by the field} \quad (1)$$

and when

$$\Sigma \chi_{Mf} < \Sigma \chi_{Mi} \text{ the rate of reaction is retarded by the field} \quad (2)$$

while with

$$\Sigma \chi_{Mf} = \Sigma \chi_{Mi} \text{ no change within and without the field} \quad (3)$$

where

$\Sigma \chi_{Mf}$ = the sum of the molecular susceptibilities of the final products,

and

$\Sigma \chi_{Mi}$ = sum of the molecular susceptibilities of the initial substances.

In all the experiments considered so far the case of reduction of ferric chloride with aluminium (1 b) stands out an apparent exception for in this case AlCl_3 is diamagnetic, and as in the case of zinc the reaction is expected to be retarded. Contrary to this, however, the reaction is accelerated. We can, however, say that in the cases where the metal itself is paramagnetic the reaction is accelerated. For both Fe and Al are paramagnetic. Zn is diamagnetic and the action is retarded. But the data at present are too meagre to say this. Moreover, the complexity of the reaction and the side reactions preclude any closer investigation. In the reactions 7 and 8, it has not been possible to evaluate the susceptibilities of the final products as the values for Fe(OH)_2 and Co(OH)_2 are still unknown. As, however, the rest of the reactants, except $\text{Fe(SO}_4\text{)}$ and Fe(OH)_2 in 7 and CoSO_4 and Co(OH)_2 in 8 are all diamagnetic, the values for Fe(OH)_2 and Co(OH)_2 or for the corresponding oxides should be very nearly equal to that of FeSO_4 and CoSO_4 respectively. In these cases the relation (3) above seems to hold good.

In the introductory part of this paper reference has been made to a recent paper of Weigle, who has shown mathematically that in the case of a solution placed in a magnetic

field, the concentration of the solution within and without the field is not the same, although the numerical value of this change is very small, being of the order of 10^{-5} for NiSO_4 in a field of 10,000 gauss. Yet, it is easily seen that in a mixture of two ions, say, Fe'' and Fe''' , the numerical ratio of Fe'' to Fe''' will be quite appreciable and thus is likely to influence the velocity considerably.

Weigle's equation simplified for the case of a mixture of liquids is

$$\frac{n}{n^0} = e^{\frac{\sigma H^2}{2kT}},$$

where n^0 is the concentration when $H=0$ and n the concentration inside the field of strength H gauss σ is

$$\frac{\chi_M}{N};$$

χ_M being the molecular susceptibility and N Avogadro's number. k is Boltzmann's constant and T the absolute temperature.

We may now consider our reactions in the light of this equation. For this purpose the reaction 4 can be written in the skeleton form thus :



$$\chi_M \text{ for } \text{CrO}_3 = 0.75 \times 100 \times 10^{-6} = 75 \times 10^{-6}$$

$$\text{therefore } \sigma_1 = \frac{75 \times 10^{-6}}{60.6 \times 10^{22}} = 1.25 \times 10^{-28}$$

$$H = 1300 \text{ gauss}, T = 297 \text{ abs.}, K = 12.5 \times 10^{-17}$$

$$\begin{aligned} \text{therefore } \frac{n_1}{n_1^0} &= e^{28 \times 10^{-8}} \\ &= 1.000,000,003 \text{ nearly.} \end{aligned}$$

Similarly for Cr_2O_3

$$\begin{aligned} \frac{n_2}{n_2^0} &= e^{10.52 \times 10^{-8}} \\ &= 1.000,000,1 \text{ nearly.} \end{aligned}$$

If we assume that the concentrations outside the field are the same, i.e., $n_1^0 = n_2^0 = n^0$ (say)
we have

$$\frac{n_1 - n_1^0}{n_2 - n_2^0} = \frac{3}{100}.$$

That is the final product of reaction Cr_2O_3 tends to concentrate about 33 times more in the field. As the field near the poles is strongest, it is probable that the largest concentration of the more paramagnetic ions will be found in their vicinity, leaving their concentration less in the rest of the space. As this space will in all probability be more extensive, the velocity of forward reaction in this space will certainly be greater, and we might reasonably expect a net increase in the forward velocity from this point of view alone. This increase in the forward reaction would always take place when molecular susceptibility of the final products is greater than that of the initial. In the reaction considered above, only the concentrations of the chief constituents have been considered. The presence of other ions is also likely to affect the results. But wherever large changes in the susceptibility of the chief constituents are involved and the other ions are either feebly para- or diamagnetic, we may be justified in neglecting them and considering only those having large paramagnetic values.

In the present investigation great care was taken to select only those reactions which involve large changes in susceptibility, for it is only in those cases that changes in the velocity would be large enough to be detected chemically.

In the above consideration, based on Weigle's equation of changes in the concentration near the strongest parts, we find an explanation also for observations of Parker and Armes*, who noticed that in their reaction by keeping the liquid under constant stirring the change in velocity became much less. This was also noticed by us and so in our experiments particular care was taken to stir the solution only at fixed intervals, and only as much as was necessary to ensure a more or less homogeneous progress of reaction. It has also been noticed in confirmation of the above that in those strongly paramagnetic salts where precipitates are formed, the precipitate has a strongly marked tendency to concentrate near the poles.

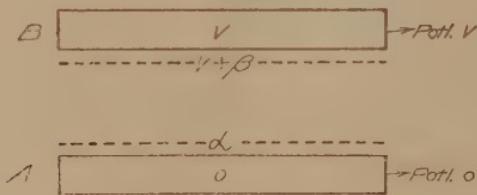
* Parker and Armes, *loc. cit.*

University Chemical Laboratories,
University of the Punjab,
Lahore, India.
29th January, 1929.

L. *On the Variation with Temperature of Contact Electromotive Forces.* By J. J. McHENRY, M.A., M.Sc.*

IN a previous paper † experiments were described which suggested that the contact difference of potential between clean metals was proportional to the absolute temperature. In most of the work the metals used were copper and zinc, but experiments were also made with copper and aluminium and also with copper and tin, in which the contact potential differences were shown to obey approximately the above law. The metal surfaces experimented with were made as clean as possible by scraping with steel tools or emery paper, and were in contact with dry air at atmospheric pressure. The method used was the "null ionization method." This method, which had previously been used by Greinacher ‡

Fig. 1.



and Anderson & Bowen §, was used in some of the experiments described in this paper and the older condenser method was used also. A short description of both methods will now be given.

Consider two metals A and B (fig. 1). Let the interior of the metal A be at zero potential, and let it be insulated. Then a point just outside the metal is at a different potential α . This potential α is called by workers on photo-electricity the "intrinsic potential" of the metal A and is shown by them to be negative. Let the second metal B be maintained at a potential V and let its intrinsic potential be β . Just outside the metal B, the potential is then $V + \beta$. In general there is a difference of potential between the regions just outside the metals, or in other

* Communicated by the Author.

† Phil. Mag. iii. April Suppl. 1927.

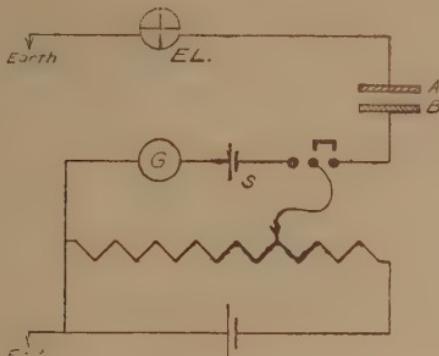
‡ Ann. der Physik, xvi. p. 708 (1906).

§ Proc. Phys. Soc. Lond. xxiii. pt. 5 (1911).

words, there is an electric field in the space between the plates. If $V=0$, this potential difference is $\alpha-\beta$ and is called the contact potential difference between A and B. If $V=0$, the potential difference in the field between the plates is $\alpha-\beta-V$, and therefore vanishes when V is equal to $\alpha-\beta$, that is, when V is equal to the contact potential difference. In this case if there is ionized air between the plates no current flows, so that the insulated plate A remains at zero potential, and if joined to a quadrant electrometer in the usual way, no motion of the electrometer needle takes place.

In the condenser method, when $V=\alpha-\beta$, and there is no field between the plates, a relative motion of A and B produces no change in the potential of A, so that if V be

Fig. 2.



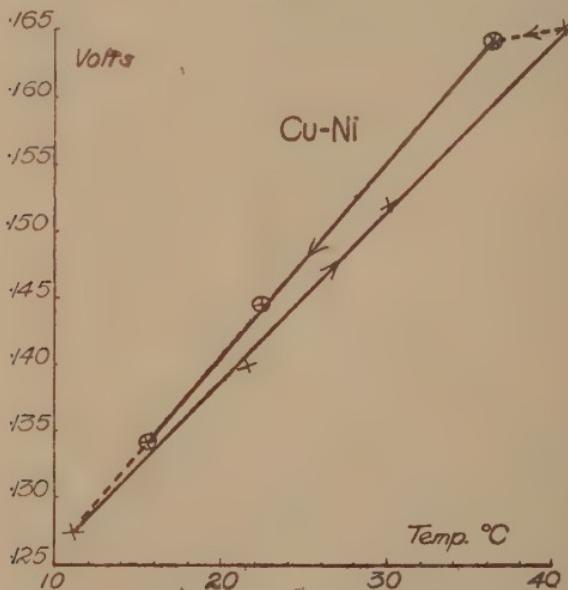
altered until this is so, V is equal to the contact potential difference. In our experiments V was varied by means of a potentiometer, the readings of which were checked against a standard cell. The electrical connexions for the "null ionization method" and the "condenser method" are shown in fig. 2, in which G is a sensitive galvanometer and S the standard cell.

In many of the experiments described in the previous paper (*loc. cit.*), the electromotive force of contact (E) varied in such a way with temperature that E was approximately equal to $T \frac{dE}{dT}$ where T is the absolute temperature.

The graph of E against T was in general a straight line which if produced would pass through a temperature near absolute zero. In other experiments deviations from the above law were noticed and in particular it was

frequently observed, when the cell was warmed and cooled, that the graph of E against T instead of being straight was a closed loop, the values of E being smaller for ascending temperatures than for descending temperatures. This effect is shown in fig. 3 with the metals copper and nickel and in its most marked form in fig. 4 with the metals copper and tin. The arrows indicate the order in which the readings shown in the graphs were taken. In all these cases a copper vessel was the outer electrode and it was completely covered with water. The water was slowly heated by a Bunsen burner placed underneath, and

Fig. 3.

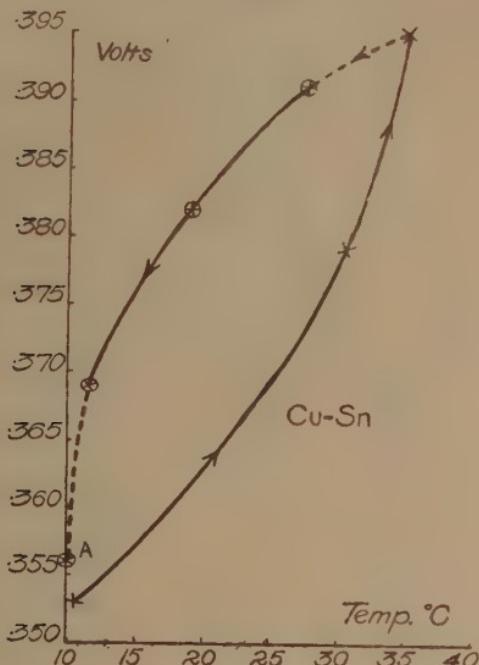


the temperature of the copper vessel and that of the inner electrode taken to be the same as that of a thermometer in the water. In general about eight readings were taken, at intervals of approximately one hour. It was thought that the "hysteresis" effect illustrated in figs. 3 and 4 might be due to a difference in temperature between the inner and outer electrodes, in spite of the time allowed for temperature equilibrium in the cell. If the inner electrode was appreciably cooler than the outer when the cell was being warmed and warmer when the cell was being cooled, the curved nature of the graphs shown could be explained. It was therefore thought advisable to change the mode of

experiment, and to alter the temperature of one electrode only. In this case $\frac{dE}{dT}$ is the rate of change of the intrinsic potential of one metal with temperature.

The new apparatus is shown in fig. 5, which is drawn to scale. The outer electrode is a stout copper vessel and lid, and the inner electrode is hollow so that its temperature could be varied by pouring in warm or cold water. A thermometer placed in this water and resting on the

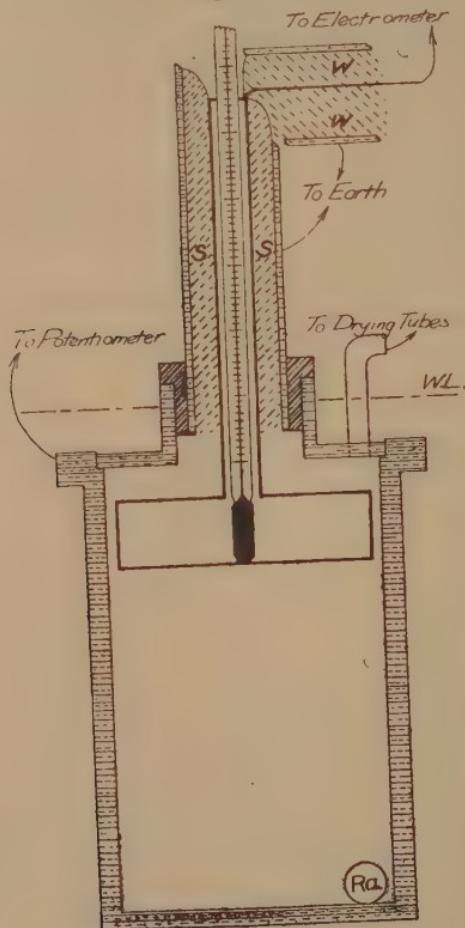
Fig. 4.



bottom of the inner electrode gave its temperature: The outer vessel was immersed in water, and its temperature taken with a second thermometer. The upper level of the water is shown dotted in the figure. A tube running from the copper vessel was connected with drying tubes containing metallic sodium and calcium chloride. Inner electrodes of copper, zinc, and aluminium were used. The air inside was ionized by a tube of radium bromide which was contained in a small jacket of copper. The inner electrode was joined by a soldered connexion to the screened electrometer leads. In the case of aluminium a platinum wire was welded to the aluminium vessel and

the wire soldered to the leads. The upper portion of the inner electrodes passed through an earthed copper tube, being insulated from the latter with sulphur which is marked S in fig. 5. Care was taken to fill up as much as possible of the space between the leads and the earthed tubes surrounding them with paraffin wax, so that

Fig. 5.



ionization of the air outside by the γ -rays which penetrated the copper vessel and lid might not affect the readings. The outer vessel was about 6 mm. thick, and the lid about 3 mm.

In experiments made with this new cell, when the inner electrode contained warm water, its temperature dropped slowly owing to loss of heat to the cold outer vessel, and

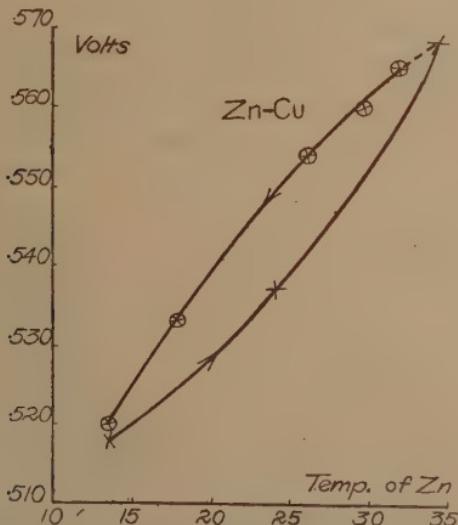
in consequence its temperature was taken before and after each reading and the mean of these temperatures, seldom differing by more than two degrees, was taken as the temperature of the inner electrode when the potential difference was being read.

Table I. and fig. 6 show the results of an experiment in which the inner electrode was made of zinc. The copper was kept at constant temperature, and the zinc was warmed and cooled. All temperatures are given in degrees centigrade.

TABLE I. (Fig. 6.)

Temp. of Copper.	Temp. of Zinc.		Mean temp. of Zinc.	E.M.F. (Volts).
	Before.	After.		
13.5	13.5	13.5	13.5	.518
13.4	24.5	23.4	24.0	.537
13.5	36.4	32.0	34.2	.568
13.5	33.5	32.1	32.8	.565
13.7	30.3	29.0	29.7	.562
13.4	26.6	25.5	26.1	.555
13.5	18.1	17.6	17.9	.533
13.8	13.5	13.5	13.5	.520

Fig. 6.



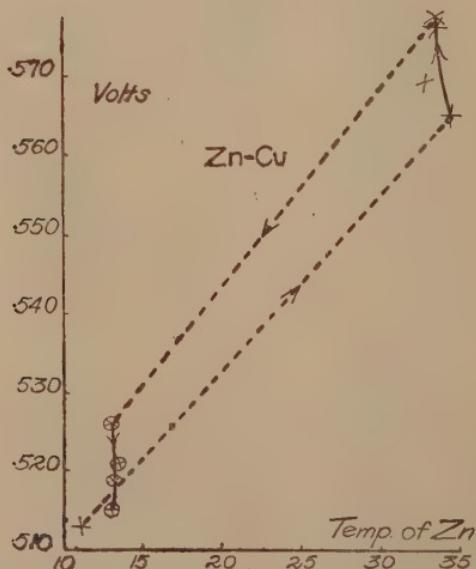
It will be seen from fig. 6 that the graph showing the relation between the e.m.f. and the temperature of the

zinc is a closed loop and not a straight line, so that the "hysteresis" noticed in the previous experiments is real, and cannot be explained by assuming an error in reading the temperature of the zinc electrode. The contact difference of potential, in these experiments where the

TABLE II. (Fig. 7.)

Temp. of Copper.	Temp. of Zinc before reading E.	Temp. of Zinc after reading E.	Mean Temp. of Zinc.	E.
12.1	12.1	12.1	12.1	.513
12.2	35.2	33.7	34.5	.565
12.2	34.5	32.4	33.5	.576
12.3	34.1	31.7	32.9	.569
12.4	34.6	32.1	33.4	.577
12.7	13.0	13.0	13.0	.526
12.7	13.2	13.2	13.2	.521
12.7	13.1	13.1	13.1	.519
12.8	13.0	13.0	13.0	.515
12.8	12.93	12.9	12.9	.515

Fig. 7.



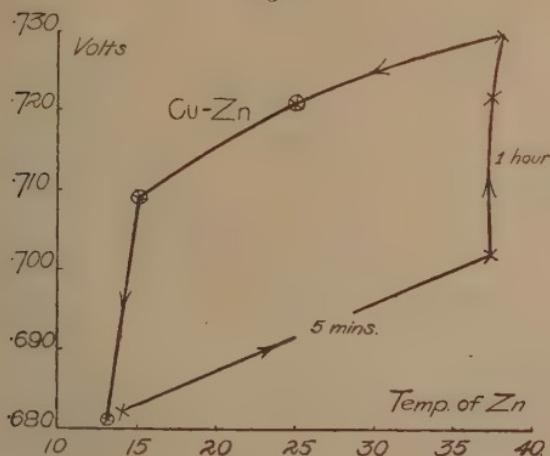
surfaces are in contact with air, depends not only on the temperature, but also on the previous treatment of the surfaces, and when the temperature of the metals is

altered the resulting change in the contact potential difference is not immediate but takes a very appreciable time to be complete. These facts are more clearly shown in other experiments, the results of which are given in Tables II. and III. and illustrated in figs. 7 and 8. In these readings the value of E , the contact potential difference between copper and zinc, was taken when both metals

TABLE III. (Fig. 8.)

Temp. of Copper.	(Mean) Temp. of Zinc.	E .	Time between Readings.
14.0	14.1	.682	
14.0	37.5	.702	
14.3	37.6	.722	1 hour
14.8	38.2	.730	
14.9	25.0	.721	—
14.9	15.2	.709	—
13.2	13.2	.681	taken next day

Fig. 8



had been for some time at room temperature. Then the temperature of the zinc inner electrode was suddenly raised about 20 or 30 degrees, and maintained at this higher temperature for an hour or two. During this time the values of E were read, the first reading being taken about five minutes after the zinc was warmed. Cold water was then poured into the inner electrode to replace the warm

water, and with both electrodes at room temperature further readings of E were taken at intervals.

It is of interest to compare figs. 7 and 8. In the former the value of E is for all temperatures considerably lower than in the latter, so that in fig. 7 the zinc surface is somewhat "aged" or tarnished. In this case the response of E to a change of temperature is greater and quicker than for the cleaner metal of fig. 8. In fig. 7 the value of $\frac{dE}{dT}$ for a quick change is .0023 volt/degree, and for a slow change .003 volt/degree. In the experiment illustrated in fig. 8, and made with exactly the same apparatus as in fig. 7, the corresponding values of $\frac{dE}{dT}$ are .00085 and .0021 volt/degree.

Fig. 9.

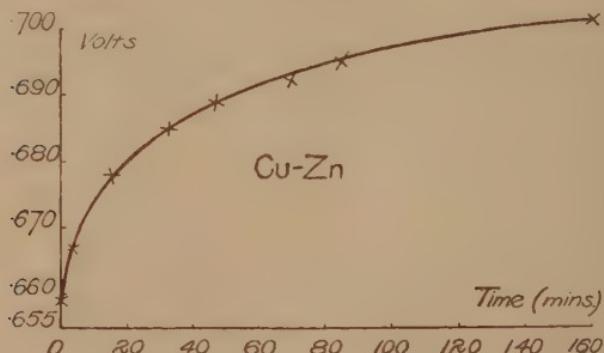
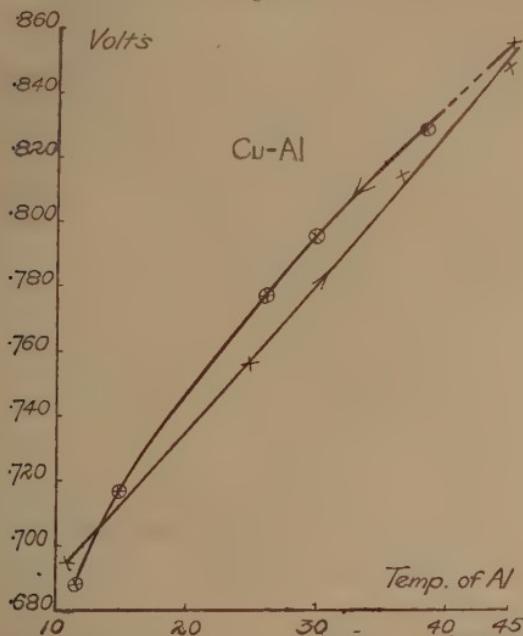


Fig. 9 shows how the contact potential difference between zinc and copper changes with time when the zinc has been suddenly warmed and kept at the higher temperature. E was read at room temperature. Then warm water was poured into the zinc electrode and the temperature raised to about 40°C . E was again read as quickly as possible, the first reading being completed about four minutes after the warm water was poured in. The temperature of the zinc was maintained at about 40°C . for nearly three hours and the e.m.f. measured every few minutes. The graph shows that complete equilibrium at the higher temperature is not attained even after 160 minutes.

In all the experiments, the cell returns after heating to its original state, the value of the e.m.f. at room temperature being the same at the end as at the beginning of the

experiment. The changes observed cannot, therefore, be explained by oxidation or reduction, as such chemical actions would hardly be reversible. On the other hand, since the value of E in all the experiments is less than the value obtained immediately after the metals are cleaned, it is possible that the effect of warming the metals is simply to drive out adsorbed gas or vapour, and that this change is reversed on cooling. This would agree with the result mentioned above that the change with temperature is smaller for clean metals than for metals which are more "aged." If this explanation is correct, heating would cause

Fig. 10.

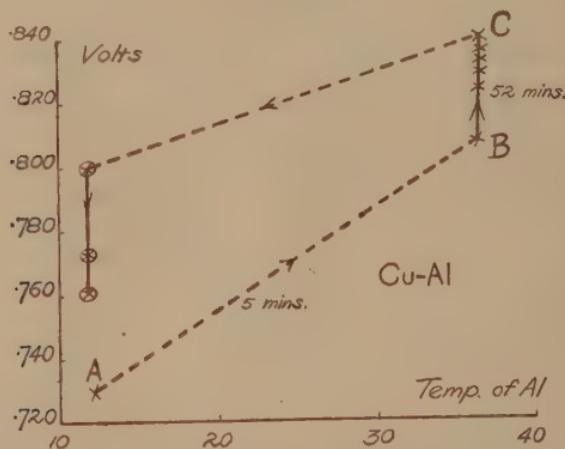


no appreciable change of the contact potential difference between copper and zinc if these could be experimented with immediately after being cleaned, and before the adsorbed layer of gas or vapour is formed. This point is referred to later in this paper.

The behaviour of aluminium is similar to that of zinc, and is illustrated in figs. 10 and 11. In the former the copper was kept at constant temperature, and the aluminium inner electrode warmed and cooled and readings of the e.m.f. taken at different temperatures between 11° C . and 46° C . The whole series of ten readings was

taken in about two hours so that approximately twelve minutes elapsed between one reading and the next. The points lie so nearly on a straight line that the hysteresis effect might easily escape detection, but it is shown to be present in the experiment illustrated in fig. 11, which gives the readings taken with exactly the same apparatus three days later. The time that passed between pouring of the warm water into the aluminium electrode and taking the first reading was about five minutes, and the readings between B and C in the graph took about fifty-two minutes.

Fig. 11.



The value of $\frac{dE}{dT}$ from fig. 10 is $.0047$ and in fig. 11 $.0045$ volt/degree for a slow change. For a sudden change (AB) in fig. 11 $\frac{dE}{dT}$ is $.0032$ volt/degree.

Zinc and aluminium become more electro-positive when heated, since the e.m.f. of the cell then increases. In other words, the absolute value of their intrinsic potentials diminishes as the temperature increases, by $.0045$ volt/degree in the case of aluminium and by between $.0021$ and $.003$ volt/degree in the case of zinc. Experiments made with the hollow copper electrode showed that this metal became more electro-negative when heated, and by $.00074$ volt/degree. In these experiments the inner electrode of copper was a few hundredths of a volt electro-positive to the outer copper vessel. Heating the inner vessel caused the e.m.f. to diminish, whereas in the

experiments with zinc and aluminium heating the inner electro-positive electrode caused the e.m.f. to increase. On the other hand, when the outer electro-negative electrode was heated the e.m.f. increased, so that the outer copper vessel also became more electro-negative when heated, and by .00067 volt/degree. Heating the cell as a whole caused practically no change in the e.m.f., a rise of temperature from 15° C. to 39° C. causing the e.m.f. to increase from .0297 volt to .0305 volt.

The fact that copper becomes more electro-negative when heated, whereas aluminium and zinc become more electro-positive, is very striking, no matter to what causes we attribute the changes.

Surfaces under oil.—Condenser method.

We have mentioned as a possible explanation of the hysteresis effect noted with zinc and aluminium that the whole or part of the change of the contact effect with temperature which occurs with these metals, may be simply due to the removal of surface impurities such as adsorbed gas or water molecules. If this explanation is correct the contact potential difference between two metals should become independent of temperature when all the surface impurities are removed, and this constant value should be the same as that between two freshly cleaned metals. In our experiments the temperature could not be raised above about 50° C. owing to the use of wax in sealing the cell. It was, however, generally noted that the nearer the observed value of the e.m.f. was to that obtained with freshly cleaned metals, the smaller was the change on the e.m.f. with temperature. In illustrating this point we give the values of E and $\frac{dE}{dT}$ for zinc and copper in a number of experiments in which both metals were heated.

TABLE IV.

E.M.F. Zn—Cu at 12° C.	$\frac{dE}{dT}$
.565	.00213
.693	.00195
.716	.0014
.706	.0015
.703	.0011

In one experiment with copper and tin, a clean pair of surfaces seems to have been realised. The e.m.f. at 13.3°C . was .471 volt and on warming the cell this value increased by about .0012 volt per degree. When a temperature of 41°C . was reached the value of E was .504 volt. On cooling the cell to 31°C . and further to 11.8°C ., E remained practically unchanged at .505 and .503 volt. The next day, at 12°C ., the e.m.f. was .5015 volt, so that in the cooling part of the experiment the value of $\frac{dE}{dt}$ was practically zero, and the metals clean as indicated by the high value of the e.m.f.

We shall now give an account of attempts made to produce clean metal surfaces and to keep them from tarnishing. The metals were cleaned in air and then immediately placed under liquid paraffin. In some cases the metals were cleaned under the paraffin so that the new surfaces did not come into contact with air. The potential difference of contact was then measured by the condenser method. In an experiment where the electrodes were an aluminium plate and a copper vessel the potential difference at 17°C . was at first .97 volt. On heating the apparatus to 41°C . this p.d. fell to .94 volt, and fell further to .80 volt when the cell was cooled to 16°C . At this stage further heating and cooling showed that the surfaces seemed to have become steady, as the graph of the contact p.d. against temperature became a straight line, the value of $\frac{dE}{dT}$ being .0036 volt/degree.

The apparatus was then left standing for two days and when experimented with at the end of that time the surfaces were found to have changed considerably. The p.d. had decreased to .58 volt at room temperature. At this stage the mere mechanical disturbance of the oil necessary in taking readings by the condenser method caused the measured value of the p.d. to increase from .58 volt up to a final steady value of .70 volt. On warming the apparatus the relation between the p.d. and the temperature again became nearly linear over the same values as were found in the experiment of two days before. The value of the p.d. at 62°C . was .965 volt. Further heating made the oil conducting and at a temperature of 112°C ., using a method similar to the ionization method,

the p.d. was found to be 1.074 volts, which is approximately the value obtained by other experimenters with newly cleaned aluminium and copper. The melting of the sulphur prevented us from warming the cell still further.

It will be seen, then, that the ageing or tarnishing of the metal surfaces takes place under the oil just as readily as in air, and the experiments gave no definite answer to the question whether the changes of the p.d. observed with changes of temperature were due to the removal of surface impurities or not. Drying the oil for a long time with sodium wire made no difference, the metals could not be made to keep their initial high value of the contact p.d.

Discussion of Results.

Before discussing the results, it is desirable to give an account of the work of other experimenters. In particular, we shall refer to papers by Erskine Murray*, Burbridge†, and Millikan and Winchester‡.

In Erskine Murray's experiments the condenser method was used. The temperature of one plate of the condenser was varied, that of the other plate being kept constant. The following table gives some of his results.

Metal.	Treatment of Surface.	Range of Temp. used.	P.d. agst. Gold plate at 16° C. (volts)-	Variation of p.d. for a rise of 1°C.
Al.	Polished on glass paper	16-50	1.10	+ .0043
Al.	Waxed ...	16-40	.98	+ .0032
Al.	Washed Alcohol...	—	1.30	+ .0045
Zn.	Cleaned glass paper73	+ .0013
Sn.	Cleaned glass paper52	- .0010
Ag.	Cleaned glass paper12	- .0007
Cu.	Cleaned emery ...	16-30	.04	Small
Cu.	Cleaned emery ...	30-60	—	+ .0015
CuO.	—	—	- .11	- .0016

Erskine-Murray does not mention any hysteresis effect.

The value of $\frac{dE}{dt}$ for aluminium, + .0045 volt/degree, is the same as that obtained by us for a slow change. The value .0013 volt/degree given by him for zinc is intermediate

* Phil. Mag. xlv. p. 398 (1898).

† Burbridge, Phys. Rev. 2nd Series, ii. Sept. (1913).

‡ Millikan and Winchester, Phil. Mag. xiv. p. 201 (1907). Millikan, Phys. Rev. 2nd Series, vii. p. 18 (1916). Or "Atomes et Électrons" (Institut International de Physique Solvay (1923)).

between the values obtained by us for slow and rapid changes. He does not seem to have put the metals through a cycle of temperature. He states that the changes are not due to alteration in the amount of oxygen in the plates.

Burbridge (*loc. cit.*) also used a variable condenser method and the following table gives his results.

Metal.	Range of Temp.	Change of p.d. for 1° C.
Cu.	20—70	.00050
Ni.	20—90	.00086
Zn.	20—55	.0024
Sn.	20—45	.00096
Sn.	45—90	.0020
Al.	20—40	.0011
Al.	40—70	.0023
Al.	70—90	.0036

Burbridge states that oxidation effects were noticeable which have to be allowed for in estimating the changes due to rise of temperature. He does not mention any differences in sign between the temperature coefficients of the various metals, nor does he seem to have observed any "hysteresis" effect. It is possible that the latter may have been present in his experiments with tin and aluminium as the graph of temperature against potential difference given by him for these metals is curved.

Millikan (*loc. cit.*), who worked with metal surfaces in a vacuum, states that all photo-electric phenomena are independent of temperature, and in particular, that the "stopping potentials" are independent of temperature. The stopping potentials are the differences of potential which, maintained between the illuminated metal and the Faraday cylinder, are sufficient to prevent photo-electrons from reaching the cylinder. He deduces that the contact differences of potential are independent of temperature, but his experiments and those of Richardson & Compton * and Page † confirm the existence of a real contact or Volta effect between metals. It is of interest, also, that the values of the contact differences of potential obtained by these experimenters who worked with metal surfaces in a vacuum are practically the same as those got by experiments performed with metal surfaces in air.

* Phil. Mag. **xxiv.** p. 592 (1913).

† Amer. Jl. of Science, **xxxvi.** p. 501 (1913).

In connexion with Millikan's experiments, it may be pointed out that if the stopping potentials are independent of temperature, this merely proves that the intrinsic potential or voltaic character of the Faraday cylinder does not alter. The Faraday cylinder is made of oxidized copper. The "stopping potential" depends only on the frequency of the light used and on the nature of the Faraday cylinder or receiving electrode, and is independent of the nature of the illuminated metal. This was proved experimentally by Page (*loc. cit.*) and verified by Millikan. It would seem undesirable to assume that the result proved for a copper-oxide surface holds also for all pure metals.

Experiments were performed by us to determine the temperature coefficient of the intrinsic potential of a surface of copper oxide. It was found that a rise of temperature of 1°C . caused the surface to become more electro-negative, by between $\cdot0012$ and $\cdot0008$ volt. A rise of temperature of 100°C . should therefore cause a change of about one-tenth of a volt in the stopping-potentials in Millikan's experiments. The least change that could be detected in his experiments was a change of "some hundredths of a volt."

On the one side then, Millikan's experiments and the electronic theory of O. W. Richardson * demand that the intrinsic potentials of metals and the Volta effect are independent of temperature if changes of the order of those met with in thermo-electricity be neglected. On the other hand, the application of thermodynamics to the ionized air cell † and a more direct thermodynamical proof by Foa ‡ supported by the experiments of Erskine-Murray, Anderson, Burbridge and the author, indicate a much larger variation with temperature of the Volta effect. It must be emphasized that the latter experiments were all performed with metal surfaces in contact with air.

In connexion with the result obtained by us that the voltaic character of the metals zinc and aluminium takes an appreciable time to respond to temperature changes, some reference is relevant to the experiments of Perucca § and Bibesco ||. From his experiments on the voltaic

* 'The Emission of Electricity from Hot Bodies.'

† Anderson, Proc. Phys. Soc. Lond. xxiv. pt. 2 (Feb. 1912).

‡ *Nuov. Cim.* iii. (1926) or *Journal de Physique*, Mars 1927, p. 152 D.

§ Phil. Mag. (Feb. 1928) or *C. R.* clxxv. p. 519 (1922).

|| *Annales de Physique* (Mai-Juin, 1925).

character and surface tension of mercury, Perucca finds that a mercury surface, freshly formed in *vacuo*, attains immediately a stable state of least potential energy in which the surface tension and intrinsic potential have definite values. When the surface is formed in a gas the surface tension and intrinsic potential are initially very high, but change and reach the values of the vacuum-formed surface after the lapse of a time which increases with the gas pressure. He concludes that the bombardment of the surface by the gas retards the orientation of the mercury molecules necessary for the production of a stable condition of least surface potential energy. The presence of the gas, however, does not alter the final condition of the surface. A similar reason may explain the lag or "hysteresis" effect noted in this paper.

In conclusion, taking the values of the changes in the intrinsic potentials of aluminium, zinc and copper found in our experiments, we can deduce the changes in the contact potential difference between two of the metals when both are heated or cooled. The temperature coefficients of the intrinsic potentials of Al, Zn, and Cu were found to be (taking the maximum values) +·0047, +·0030, and -·0007 volt per degree centigrade respectively. The contact potential difference between aluminium and copper should therefore increase by ·0054 volt per degree, and that of zinc and copper by ·0037 volt per degree. Consequently, calling the contact potential difference E , and the absolute temperature T , the value of $T \frac{dE}{dT}$ for Al—Cu at 17° C. would be 1·57 volts and the value for Zn—Cu ·97 volt. The value for $\frac{dE}{dT}$ obtained from these experiments does not, therefore, satisfy the equation $E = T \frac{dE}{dT}$, as the experimental values of E for Al—Cu and for Zn—Cu are generally found to be for new surfaces about 1·1 volts and ·7 volt respectively. The experimental value of $\frac{dE}{dT}$ is, however, of the same order of magnitude as that given by the equation.

The experiments performed with aluminium and copper under liquid paraffin are in better agreement with the equation, but the "ageing" of the surfaces which takes

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place even under the oil renders the experiments unsatisfactory.

Summary.

The changes with temperature of the voltaic character of aluminium, zinc, and copper were examined, the metal surfaces being in dry air at atmospheric pressure. For a slow rise of temperature of 1° C. aluminium and zinc become more electro-positive by .0047 and .003 volt respectively. Copper, on the other hand, becomes more electro-negative by .0007 volt/degree.

The changes with temperature of the voltaic character of the metals are not instantaneous, but take several hours to be complete.

It is found that $\frac{dE}{dT} > \frac{E}{T}$ where E is the contact difference of potential between a pair of the metals and T the absolute temperature. Taking the maximum values of $\frac{dE}{dT}$, it is found that they are roughly 40 or 50 per cent.

higher than the values of $\frac{E}{T}$.

Experiments are described with metal surfaces under liquid paraffin in which the condenser method was used. The results are compared with those of other experimenters.

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LI. *The Quantum Theory as a Problem in Lines of Force.*
By C. D. NIVEN, Ph.D., Toronto *.

I. *General Introduction.*

THE tendency in physics at the present day is to make an assumption, and from that assumption to work out a mathematical theory. Following such a practice, Professor Planck discovered the Quantum Theory at the beginning of the present century ; more recently the wave mechanics have been developed in a somewhat similar manner. Practically no attempt has been made to give a physical explanation of the Quantum Theory, and, although the

* Communicated by the Author.

wave mechanics have been strikingly successful in explaining facts, the mathematics are sufficiently involved to obscure the physics of the theory. In the following paragraphs an endeavour is made to express a point of view with regard to the Quantum Theory.

Suppose an electron be imagined as a point, having lines of force starting in all directions from it, and a proton or positive nucleus as a point on which these lines can terminate ; such a picture is practically what Faraday visualised in his theory of lines of force. When an electron is at rest in free space, the lines of force extend to infinity in all directions ; if we consider a proton brought near the electron, the lines of force will become "bunched" together around the line joining the electron and proton, with the result that fewer lines go out to infinity. Close to the electron the lines of force start in all directions, but farther out they are bent round so as to run parallel to the axis of the doublet—as the line may be termed which joins the proton and electron. The effect of bringing the electron closer up to the proton, on that part of a line of force which is near to the electron, is to make it swing round towards the direction of the axis, while the effect on the portion of the lines of force far out from the electron, and which is already running almost parallel to the axis, is to displace the line of force laterally towards the axis. When, therefore, an electron is brought near a proton, the lines of force tend to swing round and group around the axis ; when the charges are separated the lines of force are released again. If now instead of bringing charges from infinity, two balls are taken at a distance " l " apart and positive and negative charges gradually piled on to them, the effect in the region midway between the balls is similar to the effect of bringing the balls fully charged from infinite distances in either direction.

Mathematically, two simple harmonic motions at right angles are equivalent to a circular motion ; and therefore mathematical reasoning applied to the electric doublet of variable moment $el \sin nt$ was considered applicable also to the case in which the negative charge described a circle around the positive charge as centre. Although it would appear from our ideas of lines of force that there should be a similarity, yet the case of the hydrogen atom shows that an electron revolving about a nucleus does not emit

radiation. Furthermore, in the previous paragraph it has been pointed out that when positive and negative charges are piled on to two balls gradually, there is a gradual crowding together of lines of force in the region between them. In the case of the one charge revolving around the other, there is no such gradual crowding together. This crowding together seems therefore to have something to do with the emission of radiation, especially as the alternate crowding together and releasing of lines of force would resemble the condensation and rarefaction of air in the emission of sound.

In the treatment of the Hertzian oscillator the varying double $el \sin nt$ can be written in two ways $e \times l \sin nt$ and $l \times e \sin nt$. Although mathematically similar, they have different physical meanings; $e \times l \sin nt$ means that the charge remains constant throughout the motion but the length varies, and $l \times e \sin nt$ means that the length remains constant but the charge varies. If the expression $e \times l \sin nt$ be the correct way of writing the moment of the doublet then the circular motion of one charge about another might emit radiation; but if $l \times e \sin nt$ be right then the motion of one charge in a circle around another should not be connected to the motion in the Hertzian oscillator. In this communication it is to be taken that $l \times e \sin nt$ is the correct way of writing the expression for the moment of the electric doublet; the reason for this conclusion is drawn from what has been pointed out in the last paragraph, namely that the alternate crowding together and releasing of lines of force resembles the condensation and rarefaction of air in sound. Indeed, one might most easily visualise the process of radiation by imagining a "condensation" and "rarefaction" of lines of force; at the same time it must be pointed out that a "rarefaction" of lines of force simply means a condensation of lines of force in the opposite direction. Another important difference between the wave motion set up by the condensation of lines of electrical force and that set up by the condensation of air is that when the wave in the case of air passes a molecule of air, that molecule moves along with and against the direction of motion of the wave front; in the electrical case, if an electron is encountered by the wave, it moves along the direction of the lines of force, which are pointed first in one direction and

then in the opposite one, but are always perpendicular to the direction of motion of the wave front. As was pointed out when the problem of the Hertzian oscillator was treated many years ago, this transverse motion was demanded by the phenomenon of polarized light. What, however, was not pointed out at that time was that a wave of light was a true wave of condensation and rarefaction, not however of particles of æther but of lines of force. Before leaving the subject of the Hertzian oscillator, it may be of interest to quote from Hertz's own book*, where in explaining the Hertzian oscillator graphically, he writes, "But from the time $t=0$ onwards, such lines of force begin to shoot out from the poles"; and later, "At this time the electrostatic charge of the poles is at its greatest development; the number of lines of force which converge towards the poles is a maximum." From these remarks it would appear that Hertz had in view varying charge, not varying length. The two points of view are not the same, so far as the medium between the poles is concerned: for, in the case where the charge varies, when the doublet has its maximum value, the condensation of lines of force is a maximum; while, if the length varies, when the doublet has its maximum value the condensation of lines of force has its minimum value; in the latter case the maximum condensation of lines of force is reached when the doublet has moment zero; at that instant the condensation is theoretically infinite. The difference between the two cases could be illustrated by plotting density of lines of force against time. In the case where the charge varied, the curve would resemble a sine curve, but if the length varied, the curve would resemble a cosecant curve.

If the important part of the Hertzian oscillator be the condensation of lines of force between the poles, then it is clear that circular motion of one charge around another is a different type of problem, for in that case the density of lines of force remains the same but there is merely a change in direction of the lines of force; yet it would appear that if all the lines of force from the negative charge did not terminate on the positive charge, there might conceivably be some loss of energy; so in the treatment of the hydrogen atom it will be assumed that all lines of force from the electron are pulled round to terminate on the proton, when the atom is in its normal state.

* Hertz, 'Electric Waves,' chap. ix. pp. 146-147.

II. *The Bohr Model of the Atom and Emission of Light from Discharge Tubes.*

If it be assumed that the operation of the Hertzian oscillator is correctly described above, one must not apply any of the results obtained from the old theory of the Hertzian oscillator to the problem of an electron in an orbit. The case of an oscillator which has two simple harmonic motions at right angles, working similarly to a Hertzian oscillator having one simple harmonic motion, is somewhat like the case of an electron describing a rectangular hyperbola, and not like a hydrogen atom. The wave mechanics has solved most of the problems of orbits and at the present day little attention is paid to the classical methods; yet, in spite of the spectacular success of the wave mechanics, the theory has done very little towards explaining the meaning of the quantum theory. The wave mechanics method has introduced new hypotheses; working from these, results have been obtained agreeing excellently with experiment and the reality of the quantum theory has been more firmly established than ever. Unfortunately, the new hypotheses do little to elucidate the physical meaning of the quantum theory. In the following paragraphs an attempt is made to attach a physical meaning to the quantum theory, but this does not express a disbelief in the wave mechanics; the problem is approached from an entirely different standpoint, namely, to attach a physical meaning to a few of the most fundamental principles of the quantum theory.

The work of Wilson and Sommerfeld showed that the basic assumptions in dealing with the Bohr hydrogen atom should not be to quantize the energy and the angular momentum, but to put $\oint p_k dq_k = n \hbar$. Working from the Wilson-Sommerfeld conditions, one could deduce the older ones. If the conception of lines of force is to be of any use whatever, we must make assumptions of such a nature that they will lead to some of the fundamental rules for quantization and to do this it seems reasonable to employ the Ehrenfest Adiabatic Principle at this point, and in the equation $2TE_{kin} = \text{const.}$ put the constant equal to " \hbar ," and endeavour therefrom to deduce some of the rules of quantization.

When the electron in the hydrogen atom is revolving in the orbit of lowest energy level, the lines of force can be supposed as all bunched together around the line joining the electron and proton; as the electron revolves in its orbit these lines move round too and there is an angular momentum. On the Bohr assumption, we have $mav = \frac{h}{2\pi}$. Again, the kinetic energy is equal to $\frac{mv^2}{2}$,

$$\text{therefore } E_{\text{kin}} = \frac{v}{2a} \cdot mav = \frac{v}{2a} \cdot \frac{h}{2\pi}.$$

But the time of revolution

$$(T) = \frac{2\pi a}{v},$$

$$\text{therefore } 2TE_{\text{kin}} = 2 \cdot \frac{2\pi a}{v} \cdot \frac{v}{2a} \cdot \frac{h}{2\pi} \\ = h.$$

It seems as though with a given kinetic energy the lines can travel absolutely frictionlessly through the space around the nucleus, but cannot exceed a certain angular speed. The constant in Ehrenfest's equation for the case we have taken is " h ." Let us now consider an electron at infinity brought to the proton and calculate the time the lines of force starting from the electron will take to move round so that all end on the proton, compared with the time taken for the revolution of an electron about a proton as in the problem just discussed. The lines of force near the line joining the electron and proton and directed towards the proton do not move at all, while the ones pointing away from the proton have to move through an angle " π ." Therefore if it is permissible to consider all the lines taken on an average as starting at right angles to the line joining the electron and proton, for an electron to come up from infinity to the proton and then go back to infinity is like making the lines all turn through an angle " π ." In the case of the electron in the orbit, the lines all travelled through " 2π " during a complete oscillation. The energy to travel through " π " would be half that to travel through 2π and therefore if the two energies be denoted by E_∞ and E_\odot , we have $E_\infty = \frac{1}{2}E_\odot$. But from Ehrenfest's Adiabatic Principle :

$$\frac{E_\infty}{\nu_\infty} = \frac{h}{2} = \frac{E_\odot}{\nu_\odot}.$$

$$\therefore \frac{1}{2\nu_\infty} = \frac{1}{\nu_\odot}.$$

$$\therefore \nu_\odot = 2\nu_\infty,$$

that is to say, the frequency of revolution is twice the frequency of a jump from infinity ; this is very well known and has been made the basis of Bohr's correspondence principle.

The method by which this result has been reached depends on the assumption that the two frequencies are the same type of thing, and in point of fact both depend on the movement of lines of force, although of course there is a very great difference so far as an observer at infinity is concerned, as he can only perceive the frequency caused by the jump from infinity. The result, however, which we have obtained gives a clue as to how the levels in the hydrogen atom are reached. When a jump is made between the second level and the first, the frequency ν^2 is given by $\nu^2 = \frac{E_2 - E_1}{h}$. Now supposing in the second

level half of the lines of force starting from the electron extended to infinity, and half terminated on the proton ; the energy then in the region round about the proton would be $(\frac{1}{2})^2$ times what it would be when the electron had all its lines terminating on the proton, since the energy in a medium is proportional to the square of the electrical polarization. Therefore the difference of energy would be proportional to $[1^2 - (\frac{1}{2})^2]$. This energy comes from the kinetic energy of the lines of force as they sweep round to terminate on the proton. Then from the equation $2TE_{\text{kin}} = h$, $h\nu$ must be proportional to $[1^2 - (\frac{1}{2})^2]$. It is clear we could visualise the mechanism of the emission of light if we could just get a process whereby an electron could be compelled to extend a fraction of its lines to infinity and leave the remainder on the nucleus. At this point it might be of interest to refer to a paper by Professor Widdington on the discharge of electricity through vacuum tubes, as a remark is made which seems to support the mechanism of emission that is to be proposed below. Widdington remarked in his paper * : " It was inferred

* Widdington, 'Nature,' p. 506, Oct. 3, 1925.

that the main supply of electrons from the cathode arose somehow from the arrival there of positive ions originating at the edge of the negative glow." This remark therefore supports the idea that the mechanism of light emission is as follows :—An atom approaches the negative electrode to which electrons are clinging thickly ; one or more become attached to the gas atom, which is immediately repelled. On the average, after an atom has moved through the length of the mean free path, it hits another atom and becomes discharged. For example, a hydrogen atom comes, say, up to the electrode and receives one electron, and gets repelled immediately. After travelling the mean free path, say, it gets discharged. As soon as the electron it received became attached, half of the lines of force from the first electron at once extended to infinity. When the discharging takes place, the electron which remains with the proton has half of its lines extending to infinity and at once gets readjusted to its normal state by the lines sweeping round to terminate on the proton. There are obviously serious objections to the mechanism, because if lines of force came in from infinity, did not some go out in their place ? How this difficulty can be overcome is not clear to the writer, but if it can be the explanation of excitation in a discharge-tube would fit in with what is required to get a portion of the lines of force of an electron out to infinity. If three electrons became attached to the proton at the electrode and only one was removed by the colliding atom, then the energy change would be proportional to $\left[\frac{1}{2^2} - \frac{1}{3^2} \right]$ and so on.

This explanation of the process of light emission shows why a study of the hydrogen spectrum should give a clue as to how the other elements are constructed. The main difference is that with a normal unexcited element all the lines of force terminate on the nucleus, while an excited hydrogen atom having just the same number of electrons would have nearly all the lines of force extended to infinity.

We must now introduce the Azimuthal quantum number. It was suggested long ago that possibly when an electron revolved in a circle about a nucleus, no radiation was emitted ; when, however, it was discovered that ellipses gave energy levels of approximately the same energy as the circles, and that the eccentricity depended on the

azimuthal number, this theory was abandoned. We may, however, reconsider this theory, if we accept the proposed mechanism of electrons becoming attached and then suddenly detached. In that case we may account for the ellipses by assuming that in the case of two electrons, one of the electrons may give rise to a sort of linear motion while the other gives rise to a circular one. How the exact motion takes place is not clear, but what is meant is, that when there is only one electron, it must go in a circular orbit; when there are two both may go in circular orbits, giving an azimuthal quantum number 2, or else one may give rise to a sort of linear motion contributing nothing to the angular momentum, but merely upsetting the circular motion of the other one. On this conception the j_s quantum numbers would seem to be connected with the angular momentum, while the j_c quantum numbers would be connected with the "linear" oscillations. The j_s quantum number has been ascribed to the spin of the electrons, and it is unfortunate that this theory does not lead to that conclusion, since the application of the spinning electron theory to various problems has been very successful.

If there is any truth in the idea of electrons becoming attached and detached in the emission of light in a discharge-tube, something of the same nature should take place when band spectra are emitted; and it seems reasonable to suppose that, instead of electrons attaching themselves, charged atoms or groups of atoms attach themselves. In the case of homopolar molecules the two atoms are hard to separate and they consequently have to become attached in couples at a time.

III. *Thermal Radiation.*

The quantum theory was originally proposed by Professor Planck in order to get the energy distribution in the spectrum when light was emitted from a heated body. In Planck's treatment of the problem a number of oscillators are assumed, but it is not stated what these oscillators are; again, the reason why multiples of $h\nu$ should be taken is not clear either. It was this treatise of Planck's that originally started the idea of $h\nu$ being an entity like a corpuscle; in the first part of this communication an endeavour has been made to emphasize the fundamental

constancy of h . It appears to be the constant in the Ehrenfest's equation when one electron is considered. On the other hand, there seems to be absolutely nothing about $h\nu$ that justifies its being considered as an entity. On the contrary, $h\nu$ can have and has all values, theoretically, when we are dealing with the Planck radiation problem. The misleading part in Planck's treatise was that the equations were such that they had a summation prefix for all frequencies, and in solving, the summation could be neglected, since the solution for one frequency gave the solution for all frequencies. On the idea that when an electron is describing a circular or suitable elliptic orbit, no radiation is emitted, it is easy to see that if the electron got a blow to send it out of its path it would oscillate to and fro about that normal path and in doing so would radiate energy. Now, a solid differs from a gas in that the electrons are influenced by forces from other atoms. There must be lines of electrical or magnetic force holding the molecules together. When a solid is heated the electrons get, as it were, blows sending them out of their paths, and there are consequently changes not only in the lines of force from the nucleus of the atom but also in the lines from the neighbouring atoms to any particular electron. A reasonable way of picturing Planck's problem would be to imagine the number of electrons as the number of oscillators ; if the electrons got blows displacing them— n_1 of them getting blows with energy $h\Delta\nu$, n_2 getting $2h\Delta\nu$, and so on, where $\Delta\nu$ is a small element of frequency, the first equation would then be :

$$n_0 + n_1 + n_2 + n_3 \dots = \text{number of oscillators},$$

and second equation would be :

$$n_1 \cdot h\Delta\nu + n_2 \cdot 2h\Delta\nu + n_3 \cdot 3h\Delta\nu + \dots = \text{energy}.$$

The energy is given when the temperature is known. There would, of course, be an infinite number of ways of making the distribution—for instance, we might put all the energy into one oscillator. To get the actual distribution, Planck introduced the entropy equation

$$S = k \log W + C.$$

In this form the meaning of the equation is obscure ; but if it be written $dS = k \frac{dW}{W}$, the constant is eliminated and

the meaning of the equation can be expressed as follows : "The increase in entropy is proportional to the percentage increase in the number of ways of making the distribution." The "stable" or resultant distribution of the energy is determined by making dS zero—that is, equivalent to picking the distribution that occurs most frequently when $(n_1 + 2n_2 + 3n_3 + \dots)$ packets of energy are divided among $(n_0 + n_1 + n_2 + n_3 + \dots)$ oscillators. The reason for following up Planck's proof by the above method was because it seemed as though multiples of $h\Delta\nu$ might give some explanation why Planck needed multiples of $h\nu$, but this method does not lead anywhere. It appears hard to imagine that each oscillator has an infinite number of frequencies which Planck's original treatise seems to imply. On further consideration it appears very doubtful if we are justified in assuming the number of oscillators constant, especially as the only way multiple quanta of energy could occur like $3h\nu$ would be if three electrons and three positive charges acted as one oscillator. Yet any method in which the number of oscillators radiating $h\nu$ is counted should include this case automatically. A more reasonable method to approach the problem seems to be to take some function of ν as denoting the number of oscillators radiating with frequency ν . If we do this we can follow Professor Debye's mathematics so far, but the assumptions from which we start are different. Let $f(\nu)d\nu$ be the number of oscillators radiating with frequencies between ν and $\nu+d\nu$. Now the number of different frequencies between ν and $\nu+d\nu$ is $d\nu$. The number of different frequencies to be distributed is $d\nu$ and the number of oscillators is $f(\nu)d\nu$, and therefore the number of ways of making the distribution is

$$\frac{|f(\nu)d\nu + d\nu - 1|}{|f(\nu)d\nu - 1|d\nu}.$$

The -1 can be neglected above and below and so we get

$$W = \frac{|f(\nu)d\nu + d\nu|}{|f(\nu)d\nu|d\nu}.$$

This is practically Debye's expression. Our equations for entropy and energy can be written down, viz. :

$$S = \int_0^{\infty} k \log \frac{|f(\nu)d\nu + d\nu|}{|f(\nu)d\nu|d\nu} \text{ and } U = \int_0^{\infty} h\nu f(\nu)d\nu.$$

If $\delta S + \gamma U$ be equated to zero as Debye did, then

$$\log \frac{(1+f)}{f} = -\gamma \frac{hv}{k} \quad \text{or} \quad f = \frac{1}{e^{-\gamma \frac{hv}{k}} - 1}$$

Debye's proof cannot be followed farther, as the expressions here used are slightly different from Debye's; but the result so far as it goes seems interesting, as it is reached by making entirely different assumptions from those of Professor Debye, and because no reference is made to multiples of the quantum entity hv .

Before leaving the problem of heat radiation, it might be as well to point out why a gas should not radiate when heated. When an electron of a gas molecule receives a blow from another atom, instead of vibrating about its stable orbit, the molecule of gas moves as a whole, and so the speed of the molecules becomes increased. In the solid state this cannot occur, and the energy of the blow must be taken up by starting electrical oscillations.

IV. The Photoelectric Effect.

In the case of the photoelectric effect, the corpuscular view of the quantum theory has met with the greatest success. The size of the effect depends on the intensity of the light, while the wave-length of the light determines whether emission can occur or not. Now, if the period of the revolution of the electron be greater than the period of the motion of the lines of force of the exciting light, it is clear that the light would cause no effect, but if the frequency of the light were greater it would speed up the electrons and eventually throw them out. If the intensity were very weak the speeding up would be small. The fact that the effect starts at once can be explained by considering that all electrons may be at different positions in their orbits, and if the electron gets an acceleration at the time when it is traversing a certain part of the orbit, the force may be sufficient to throw the electron out.

V. Conduction.

If the view of thermal radiation described in this communication be correct, some light might be thrown on the process of electrical conduction. Kinetic energy of atoms, or heat, should be attributed not directly to the motion of

atoms but to oscillations in the lines of force starting from electrons. The writer's conception of a metal does not agree with the usual free electron theory ; for if some of the electrons in metals were really free they would flow to the surface and this seems unlikely ; and therefore, the opinion is favoured that all electrons stay by their atoms but travel in orbits composing uncompleted shells*. Seeing then the electronic system is not full, there is a tendency for another electron from a neighbouring atom becoming attached. If such a mechanism be correct, it fits in excellently with Benedicks' † theory of the atom of metal actually being the carrier of electricity. So far as the writer knows, Benedicks did not extend Drude's free electron gas theory to fit his model, but this can be very simply done.

If e be the charge on an electron, after adding an electron to an atom, the force repelling the atom from the negative source of potential (X) is eX . An acceleration of f , say, is acquired ; so if M be the mass of the atom,

$$M \times f = eX \quad \text{or} \quad f = \frac{eX}{M}.$$

The time that this acceleration acts is $\frac{l}{u}$, where l is distance the atom can move in the metal and u is the mean velocity of approach of two atoms due to thermal agitation. So then, v , the velocity of drift, $= \frac{1}{2}ft = \frac{eXl}{2Mu}$, provided that the velocity of drift is negligible compared with the velocity due to heat agitation—that is to say, the time is so short during which the force acts that practically no velocity is obtained. The current is equal to nev , and so the conduction is equal to

$$\frac{ne^2l}{2Mu} = \frac{ne^2lu}{2Mu^2}.$$

Now Mu^2 is simply twice the kinetic energy of the atom and the specific heat difficulty regarding the contribution from the free electrons is completely removed. The conduction

* See McLennan, McLay, and Smith, "Atomic States and Spectral Terms," Proc. Roy. Soc. A, vol. cxii. p. 76 (1926).

† Benedicks, "Beiträge zur Kenntnis der Elektrizitätsleitung in Metallen und Legierungen," *Jahrbuch der Radioaktivität*, xiii. p. 351 (1916).

can now be written $\frac{1}{4} \cdot \frac{n e^2 l u}{\alpha T}$: since u is proportional to

\sqrt{T} , l must diminish with temperature. It can easily be seen why this must be the case from what has been said in the first part of this communication, because when there is much thermal agitation the electrons get displaced from their orbits and the effective size of an atom is really larger than when the electrons are moving in their undisturbed orbits. When the temperature of the metal is very low, the speed of the atom of metal due to thermal agitation is no longer so large that the velocity of drift can be neglected in calculating the time during which the acceleration takes place and the expression obtained above for the resistance is wrong. In the limiting case where the velocity of drift is the only velocity to be considered, u could be neglected and the expression for the resistance would now be independent of temperature, which is what occurs with practically all non-superconducting metals.

In conclusion, the writer wishes to express his thanks to Professor J. C. McLennan, F.R.S., whose inspiring lectures were the source of many ideas contained in this communication, for his most helpful criticism and support.

LII. *The Polarization of Raman Lines.* By A. C. MENZIES, M.A., Lecturer in Charge, Physics Department, University College, Leicester *.

Introduction.

IN his first announcement of the discovery of the effect, Raman † stated that the scattered lines showed evidence of being polarized. That there is a difference between the various scattered lines in this respect was shown later by Raman and Krishnan ‡, and independently by Carelli, Pringsheim and Rosen §. For example, the second group of workers have investigated the effect in benzene, toluene, and carbon tetrachloride, and have shown that the lines scattered by benzene are all practically unpolarized, but

* Communicated by Prof. R. Whiddington, F.R.S.

† Ind. Journ. Phys. ii. p. 1 (1928).

‡ 'Nature,' cxii. p. 169 (1928).

§ Zeits. für Physik, li. p. 511 (1928).

that in the other two substances some lines are definitely plane-polarized, and in the same direction as that of the ordinary Tyndall scattering. (This is with the observation at right-angles to the incident light.)

The above experiments were made by putting polarizing apparatus in the path of the emergent scattered light beam. The early announcement by Raman of the polarization of the scattered radiation led the writer to make experiments on the scattering of light already plane-polarized, using a double-image prism, and observing at various angles to the incident beam. The purpose of these experiments was to see if the polarization of the Raman lines was produced during the scattering process, or whether it occurred through molecules differently orientated being excited by incident light vibrating in the appropriate plane only.

In the meantime a preliminary announcement of a result of a similar experiment has been made by Lindemann, Keeley and Hall*, who therefore take priority in this respect. The result which they announced was that in the scattering of light by carbon tetrachloride, of four scattered lines observed, one was present only in the beam which privileged the ordinary Tyndall scattering, while the other three were present in approximately equal intensities in both beams. (Observations at right angles.)

In the present paper an account is given of the results obtained by the writer in the examination of the state of polarization of the lines scattered by carbon tetrachloride at different angles, and by quartz with its optic axis at different orientations. An attempt is made to explain the polarization which occurs, and a scheme of energy-levels is put forward to co-ordinate the infra-red and Raman data for quartz.

Apparatus and Method.

As the Raman effect is still new, it is felt justified to give an account of the methods employed in greater detail than they would otherwise warrant, since such details may be helpful to others taking up the work.

The source of light was a quartz "Atmospheric Pressure" mercury vapour lamp made by Messrs. Kelvin, Bottomley, and Baird; it took 2·6 amperes at 110 volts, and was worked from an accumulator battery employed exclusively for this purpose. This burner is automatically relit if it goes out, so that it can be left to burn without attention for days or

* 'Nature,' cxxii. p. 921 (1928).

weeks. The actual source of light is approximately L-shaped with the corner rounded off, but fortunately the vertical portion is by far the stronger. This particular lamp was selected because the small size of the source was very convenient for producing from it a narrow beam to pass through the polarizing apparatus.

It was found convenient to mount the lamp in a separate room, the light entering the dark-room through a condensing lens of 6 in. diameter let into the wall. In this way a real image of the source can be formed at the centre of a spherical flask when it is required to irradiate the liquid with ordinary unpolarized light. A device, which was found very useful when focussing an image of the centre of the flask on to the slit of the spectrograph, is to let down a long glass fibre into the liquid in the flask, in such a way that it reflects the incident light, and so appears from the side as a line of light. This may then be focussed on to the slit of the spectrograph, and the fibre withdrawn at the end of the initial setting-up. When the light is initially plane-polarized before entering the flask, having passed through a double-image prism, it is essential that the two images of the source should be as near to the centre of the flask as possible with the two beams just separated. This condition can be readily judged by letting down into the liquid a strip of opal glass or other diffusing material, and as before focussing can be carried out on these images. When the final adjustments have been completed, the liquid in the flask can be replaced by a clean sample.

For the mere observation of the effect, it is not at all necessary to employ only dust-free specimens of the scattering liquid. It is naturally preferable to do so, since the dust increases the intensity of the scattered unmodified lines.

The spectrograph was a constant deviation instrument made by Hilger, and Wellington "Xpress" plates were used (H. and D. 850, black backing). In order to bring up the faintest lines, the plates were developed with "maximum energy" developer, Eastman Kodak formula.

The number of surfaces in the optical train should be kept as low as possible. There seems no particular virtue in a large flask, and if the liquid is expensive, or tends to absorb the light, a small one is preferable.

Polarization of the Carbon Tetrachloride Lines.

- (1) *Scattering of a plane-polarized beam observed at right-angles.*

The incident beam of light was horizontal, and composed

of two beams, polarized horizontally and vertically respectively.

With twelve hours' exposure a plate was obtained, showing that the scattered line $\delta\nu = 458 \text{ cm}^{-1}$ occurred only in the beam vibrating vertically, while the lines $\delta\nu = 215, 314$, were equally strong in each beam. This, as mentioned before, was the discovery of Lindemann, Keeley, and Hall. The two fainter lines at $\delta\nu = 758, 788$, seemed to be very slightly more intense in the beam vibrating vertically.

These results are similar to those of Carelli, Pringsheim and Rosen, who observed with the polarizer in the scattered beam. The simplest assumption to make then, is that the light vibrations in the incident and scattered beams and the oscillation of the CCl_4 molecule must all be parallel in the case of the 458-line. It was also observed that the polarization of 458 is more complete when the *incident beam* is polarized.

(2) Forward-scattering of a plane-polarized beam.

The foregoing experiment suggested that if the light scattered in a forward direction could be observed, the polarized line would be equally strong in each beam. This observation is obviously not possible, but it is possible to observe the light scattered obliquely.

By using a narrow diaphragm (an auxiliary spectrograph slit opened fully) and a condensing lens on to the slit, it was possible to observe the scattering at an angle of about 160° .

It was found that the lines were almost equally strong in each beam—both spectra presented the same appearance as that due to the beam vibrating vertically in the 90° experiment.

(3) Forward Scattering of an Unpolarized Beam.

It is clear from the foregoing experiment that in the forward scattering of an unpolarized beam, the line 458 will be twice as strong relatively to the other lines as in the scattering at right-angles. This was tried, and found to be the case. Two photographs were taken of the spectrum of the light scattered, under conditions as similar as possible, at 90° and at about 160° . The intensities of all the lines were considerably greater in the second case. This was thought to be due in part to the greater depth of the scattered beam. In the forward scattering the intensity of the line 458 is about twice as great as that of its near companion 315,

while in the 90° scattering it is only very slightly more intense.

It should be possible, then, to detect the polarized lines in any Raman spectrum, by the comparison of plates obtained by sideways and forward scattering, by the selection of the lines which are strengthened relatively in the forward scattering. This method may be applicable when the more direct method is not so readily applied.

Other liquids (such as paraldehyde, acetone, toluene, methylal, mesitylene, and nitromethane) were tried with similar results. (Mesitylene goes "milky" during the irradiation, with the result that the unmodified lines are greatly strengthened.)

Theory of the Raman Effect.

Two theories have as yet been proposed to account for the Raman lines. The first, proposed by Raman, is that the modified lines correspond to actual infra-red frequencies.

The second was deduced from the dispersion theory of Kramers by Langer* and Deike † independently. This theory has been applied successfully to the case of carbon tetrachloride by Langer. According to this theory the scattered lines originate in transfers from excited levels in one system to excited levels in another system of vibration of the molecule, provided that both systems have a common level. It is by no means intended to deny that some Raman lines may correspond to some infra-red frequencies, but these occur once more as differences between pairs of levels having a common-level—it can be provided by an added rotation or perhaps even a lattice vibration.

Theory of the Polarizations.

So far, the only attempt to account for the polarizations is one put forward by Raman and Krishnan ‡ very recently. Briefly, the molecule is regarded as having three sets of axes, along each of which a vibration may be set up by the incident light beam. It is then postulated that for the different vibrations, corresponding to the different modified frequencies, the response along the three axes is different. Thus the observed different stages of polarization of the lines may be accounted for.

* 'Nature,' cxxiii. p. 345 (1929).

† 'Nature,' cxxiii. p. 564 (1929).

‡ Roy. Soc. Proc. A, cxxii. p. 23 (1929).

But, as has been mentioned in the previous paragraph, in the production of the Raman line, two vibrations are concerned rather than one, the energy of the Raman line corresponding to the difference between the energies of the two vibrations.

It is here suggested that a possible explanation (in the sense of a mechanical model) of the polarizations can be got by considering the different systems to correspond in fact to actual vibrations of the molecule. Any transition from a level in one system to a level in another system corresponds to a change in the mode of vibration of the molecule, *i.e.*, a transfer of energy of vibration from one mode of vibration to another. Now if these different directions of vibration are parallel to one another, we may expect the light scattered to be plane-polarized, while if they are mutually perpendicular, the light scattered will be unpolarized. Intermediately, the light scattered will be partially polarized. This parallelism of the directions of vibration may account for the greater intensity, as a rule, of the polarized lines, to which Raman has drawn attention.

It is clear that if this hypothesis can be established, considerable knowledge of the spatial distribution of groups in molecules can be gained by a study of the polarization of the Raman lines.

The Raman Spectrum of Quartz.

It was thought that considerable light might be thrown on the problem of the polarization of the Raman lines by a study of the modified lines scattered by crystalline quartz from this point of view, varying the inclination of the optic axis to the direction of the incident and scattered beams. Observation was made at right-angles to the incident beam in all cases.

Three cases were dealt with. First, the optic axis coincided with the direction of scattering, secondly with the direction of the incident beam, and lastly it was placed at right-angles to both. In all cases the incident light was unpolarized. These three cases will be distinguished in what follows as (1), (2) and (3).

Observations without the Interposition of Polarizing Apparatus.

There appeared to be no difference between the spectra in the three cases, except that lines appeared in case (3) for the first time with shifts of approximately 1293 and 1369 cm^{-1} . It is possible that a repetition of the experi-

ments with longer exposure may reveal this shift in all three cases. These lines are extremely faint. Measurements of all the shifts are tabulated in Table I.

Observations of the Polarizations.

When it is realized that the optical rotation of quartz in the region of the spectrum under investigation is of the order of 45° per mm., it will be clear that an attempt to observe the polarizations of the lines in case (1) is certain to fail. Consequently only the cases (2) and (3) were so investigated, where observation was made perpendicularly to the optic axis.

As was expected, in most cases the lines were plane-polarized, and moreover, the direction of polarization in some cases turned through 90° as the optic axis was turned similarly, showing that some of the vibrations involved were fixed in direction relative to the optic axis. Other lines kept their direction of polarization fixed relative to the directions of the incident and scattered light, and independent of the direction of the optic axis, showing that the directions of the vibrations concerned were not fixed relative to the optic axis. In two cases ($\nu = 265$ and 798 cm.^{-1}) the lines were polarized in a direction perpendicular to that of the unmodified lines in both cases (2) and (3). It is difficult to see simply how this can arise (a vibration parallel to the direction of the incident beam, independent of the direction of the optic axis) without the postulation of vibrators at right-angles, as has been suggested above.

In order to simplify the presentation of the results, the states of polarization are given in Table I., together with the values of the wave numbers found by other observers. The polarizations in the two cases are given in parallel columns; " π " means that the lines corresponding to the shift are plane-polarized parallel to the direction of the unmodified lines, " σ " that they are plane-polarized at right-angles to this, and " u " that they are unpolarized. The references are to Rao *, Krishnan †, Wood ‡, Pringsheim and Rosen §, and Landsberg & Mandelstam ||. In the first case (Rao and Krishnan) the original papers were unavailable, so the reciprocals of the wave-lengths quoted in a paper by Czerny ¶ are given.

* Ind. Journ. Phys. iii. p. 123 (1928).

† 'Nature,' cxxii. p. 506 (1928).

‡ Phil. Mag. vi. p. 742 (1928).

§ Zeits. für Physik, I. p. 741 (1928).

|| Zeits. für Physik, I. p. 769 (1928).

¶ Zeits. für Physik, liii, p. 317 (1929).

With regard to the actual values obtained for the shifts, the values obtained by the writer are probably not more accurate than about 1 per cent. The concordance is good; it seems likely that the values got by Landsberg and Mandelstam are in better agreement with the others than appears at first sight—it looks as if they had worked with a wide slit and so measured the mean of 694 and 798 as one line, and similarly for 1093 and 1157.

TABLE I.

R. & K.	Raman Frequencies.				Author.	Polarization.	
	W.	P. & R.	L. & M.			Case 2.	Case 3.
85	—	—	—	—	85	u	u
128	125	125	123	126	126	u(π)	σ
206	204	209	211	209	209	π	π
267	—	262	—	265	265	σ	σ
—	—	(351)	—	(356)	(356)	(π)	π
—	—	(405)	—	(406)	(406)	(π)	u
463	462	465	465	464	464	π	π
—	—	—	—	(530)	(530)	(σ)	(π)
—	—	(706)	—	694	694	(π)	σ
			743				
—	—	802		798	798	σ	σ
—	—	—	—	1093	1093	σ	π
1176	—	1157	1127	1157	1157	π	σ
—	—	—	—	1240	1240	(π)	(σ)
				1293	Absent.	(π)	
				1369	Absent.	(π)	

(Numbers within brackets are doubtful.)

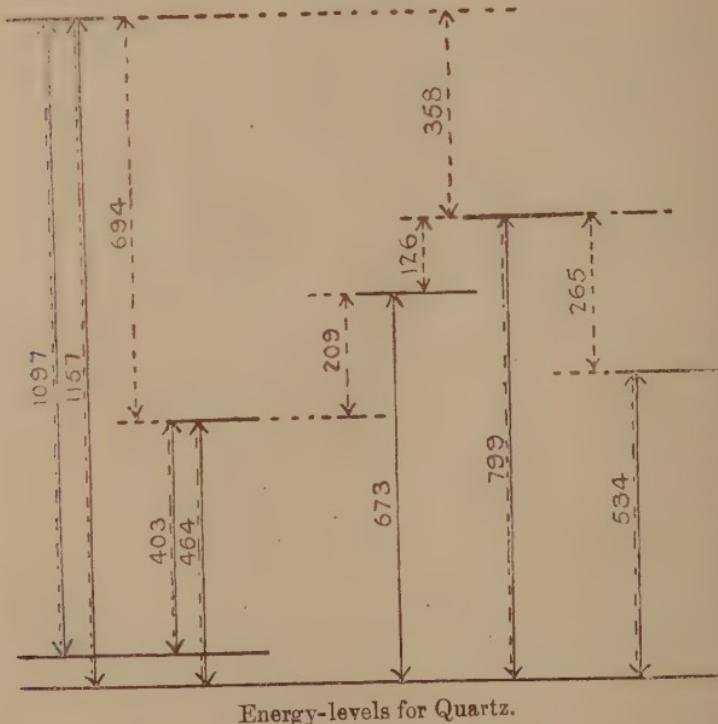
Infra-red Data for Quartz.

It was next sought to frame a system of energy-levels which should represent the Raman lines as differences between levels having a level in common. Any such scheme must naturally satisfy the infra-red data also. The data available to the writer were those quoted in Lecomte, 'Le Spectre Infrarouge,' p. 145 (reflexion experiments by Nichols, Rubens & Nichols, and Reinkober) and p. 181 (absorption experiments by Merritt and Koenigsberger,

Dreisch, Coblenz, Nichols, and Rosenthal), together with the measurements of Coblenz, Schaefer, and Schubert. It appears that the strongest infra-red vibrations are in the neighbourhood of 9μ and 21μ , so that any successful scheme would presumably involve these as fundamental vibrations.

A scheme of energy-levels is set forth in fig. 1. Here it will be noted that the very strong infra-red vibrations just mentioned are represented on the left of the diagram, in two pairs of levels, having a difference in wave-number

Fig. 1.



Energy-levels for Quartz.

of 61 cm^{-1} . In the figure, a full line is drawn to represent a transition present in the infra-red spectrum, and a broken line to represent one present as a shift in the Raman spectrum. In addition to the lines indicated in the diagram, overtones of some of the fundamental frequencies shown occur in the infra-red spectrum. These are not shown in the diagram in order to keep it reasonably small. They are given in Table II. which follows. In the first column is given the wave-length in μ calculated from the frequencies in the diagram, in the second column the values obtained

by reflexion in the infra-red, and in the third column the values obtained by absorption in the infra-red. In the fourth column is an indication of the strength of the reflexion or absorption in the infra-red, in the fifth column "o" and "e" respectively indicates that the absorption or reflexion in the infra-red applies to the ordinary ray or to the extraordinary ray, and in the last column is given the origin of the vibration in terms of the present scheme.

TABLE II.

Wave-length.					
Calculated.	I. R. Refn.	I. R. Abspn.	I. R. Int.	I. R. Poln.	Origin.
2·98	3	2·97	Weak.		$3 \times 1096 + 61$
3·04	"	3·02	"		3×1096
3·71	—	3·75	"		4×673
4·43	4·5	—	Weak.		$2 \times 1096 + 61$
4·55	"				2×1096
4·95	—	5·02	"		3×673
6·26	—	6·26	"		2×799
8·64	8·50		V. strong.	o e	Fundamental.
	8·70		"	e	
	8·90		"	o e	
9·11	9·05		V. strong.	o e	Fundamental.
12·5	12·52		Strong.	o	Fundamental.
	12·87		"	e	
14·9	14·55		"	o	Fundamental.
18·7	18·5		"		Fundamental.
	19·7		"	e	
21·6	21		V. strong.	o**	Fundamental.
24·8	26		Strong.	o	Fundamental.
	27·5		"	e	

Still unaccounted for in this scheme are three weak infra-red observations, and the Raman lines at 85, 1240, 1293, and 1369, which are all weak.

It is difficult to draw any conclusions as to the connexion between the polarization of the infra-red vibrations and the polarization of the Raman lines, owing to the ambiguity in the infra-red observations.

A scheme of energy-levels which accords rather better with the Raman observations, but considerably less well with the infra-red data, can be built up with the following as fundamental frequencies :—700, 809, 1080, 1165, and 1291. This gives as differences :—85, 126, 211, 271, 356, and 465. The merit of the scheme is that it represents the strongest Raman lines (126, 211 and 465) as differences. Its drawback is that it does not involve the very strong infra-red wave-length at 21μ as a fundamental vibration, and does include as such the wave-number 1291, which has no counterpart in the infra-red.

More exact data in the infra-red region are required to settle this problem, and also more exact measurements of the Raman lines. The plates used in the course of the present work were obtained with an exposure of three days. These measurements will be repeated with the same specimen of quartz, using a still finer slit, and giving exposures of weeks in duration. It is worth while remarking that in the infra-red experiments the exact position of the band varies often from specimen to specimen.

I am indebted to my friend and former pupil Mr. C. P. Snow, of the Physical Chemical Laboratory, Cambridge, for helpful discussion.

Summary.

Using a small source and a double-image prism, observations have been made of the light scattered by carbon tetrachloride and other liquids at 90° and at an angle of about 160° .

It is suggested that the observed polarization of the line can be explained if it is supposed that the direction of the initial vibration is parallel to that of the final vibration in the case of the plane-polarized lines, and that they are perpendicular to one another in the case of the unpolarized lines. Lines partially polarized can be explained by the inclination of the directions of vibration to one another being intermediate between the two cases.

The Raman spectrum of quartz has been measured for three different orientations of the optic axis, and the state of polarization of the lines has been investigated. Some of the scattered lines change their direction of polarization through 90° as the direction of the optic axis is similarly turned. Two lines remain plane-polarized in the customary direction (parallel to that of the unmodified lines) in spite of the orientation of the optic axis being changed, and in the

case of two other lines the direction of polarization is invariable also, but is perpendicular to the usual direction (vibration parallel to the direction of propagation of the incident light).

An energy-level diagram is given which co-ordinates the Raman and infra-red observations, and may have some real significance.

(Since the above was written, I have seen a report by Cabannes in *Comptes Rendus*, clxxxviii, p. 249 (1929), in which he gives the results of experiments with quartz similar to those described in the present paper. The wave-numbers, measured by Daure, are 129, 208, 267, 357, 403, 467·5, 700, 796, 1062, 1165, 1287. They are represented as multiples of three small numbers.

The polarization observations are less complete than in the present paper, but are in agreement with those detailed here, except for a slight disagreement in the case of the weak line 1157. Cabannes suggests that the polarizations may arise through interference due to coherent scattering.)

Physics Department,
University College, Leicester.
June 27th, 1929.

LIII. *The Fine Structure of Spectral Lines.*

By J. C. McLENNAN, F.R.S., and E. J. ALLIN, M.A.*

(Holder of a National Research Council of Canada Studentship.)

[Plate XI.]

THE work described here is a continuation of experiments previously carried out by the authors†. The plan followed in this earlier work of studying lines in the first spark spectrum of an element and comparing the structures found for these lines with the structures found for lines in the homologous series of the corresponding arc spectrum has again been adhered to and the experimental method has not been changed except in the adoption of a means of spectrum excitation suitable to the

* Communicated by the Authors.

† Trans. Roy. Soc. Can. 3, xxiii. p. 7 (1929).

metal being studied. For this reason only the source of light used need be described in detail here.

To obtain the lines in the spectrum of zinc II. and of cadmium II. the hollow cathode discharge was used. Both electrodes were hollow cylinders made of the metal and enclosed in a pyrex glass tube which was exhausted and then filled with helium. The electrodes were carefully out-gassed and the helium purified as the presence of hydrogen and other impurities prevents the production of the spark lines. The pressure of helium in the tube also had an important effect on the character of the spectrum obtained. At a pressure of $2-2\frac{1}{2}$ mm. of mercury with zinc electrodes and at a pressure of 5-1 mm. of mercury with electrodes of cadmium the lines of the spark spectrum possessed their greatest intensity. At higher pressures the helium spectrum alone was obtained and at lower pressures the arc spectrum of the metal became more prominent and the spark lines faded out. In most of the work a 30,000 volt alternating current transformer was used as a source of potential but the character of the spectrum remained unchanged when a 2000 volt direct current generator was substituted for the transformer.

For the study of lines in the spectrum of barium I. and of lanthanum II. it was the salts of the metals rather than the metals themselves that were available in quantity and it was necessary therefore to discard the method outlined above. It was decided to adopt that employed by Meggers and Burns* in the study of lanthanum I. and lanthanum II. A vacuum arc was constructed with carbon electrodes the lower of which was bored and filled with the salt of the metal under investigation. The electrodes led into the vacuum chamber through oil seals and the outside of the chamber was wound with brass tubing through which water flowed continuously to prevent the production of leaks due to the heating of the soldered metal joints. A pressure of considerably less than 1 mm. of mercury could be maintained while the arc was running. All salts of the metals were not found to be equally satisfactory. Of those obtainable barium oxide and lanthanum chloride gave the most intense spectra. A current of about 10 amperes at a potential of 220 volts was used throughout.

* J. O. S. A. (June 1927).

The results obtained are given in detail in Tables I., II., III., and IV.

TABLE I.

Results obtained for lines in the spectrum of Zn II.

Line.	Classification.	$\Delta\lambda$.	$\Delta\nu$.	Int.
6103 I.A.	$3^2P_2 - 4^2D_3$		Single	
6021 "	$3^2P_1 - 4^2D_3$		Single	
4924 "	$3^2D_3 - 4^2F_4$	{ 0 -0.071	{ 0 +292	{ 10 7
4912 "	$3^2D_2 - 4^2F_3$		Single	

TABLE II.

Results obtained for lines in the spectrum of Cd II.

Line.	Classification.	$\Delta\lambda$.	$\Delta\nu$.	Int.
6465 I.A.	$3^2P_1 - 4^2D_3$	{ 0 -0.075	{ 0 +179	{ 10 3
6360 "	$4^2F_4 - 6^2G$	{ 0 -0.055 -0.131	{ 0 +135 +323	{ 10 1 10
530 "	$3^2D_3 - 4^2F_4$	{ +0.053 0	-184 0	3 10
5337 "	$3^2D_2 - 4^2F_3$		Single	

TABLE III.

Results obtained for lines in the spectrum of Ba I.

Line.	Classification.	$\Delta\lambda$.	$\Delta\nu$.	Int.
6694 I.A.	${}^3D_1{}^0 - {}^3D_3$		Single	
6675 "	${}^3D_1{}^0 - {}^3D_2$		Single	
6595 "	${}^3D_1{}^0 - {}^3D_1$	{ 0 -0.099	{ 0 +228	{ 10 8
6527 "	${}^3D_2{}^0 - {}^3D_2$	{ +0.131 0	{ -0.308 0	{ 1 10
6499 "	${}^3D_3{}^0 - {}^3D_3$		Single	
6450 "	${}^3D_2{}^0 - {}^3D_1$	{ 0 -0.104	{ 0 +250	{ 10 1
6342 "	${}^3D_3{}^0 - {}^3D_2$		Single	
6063 "	${}^3P_1{}^0 - {}^3D_2$	{ +0.181 -0.066 0	{ -0.492 -0.181 0	{ 1 10 9
6019 "	${}^3P_0{}^0 - {}^3D_1$	{ +0.161 0 -0.082	{ -0.444 0 +0.225	{ 1 10 1
5997 "	${}^3P_1{}^0 - {}^3D_1$	{ 0 -0.066	{ 0 +0.185	{ 10 4

TABLE III. (cont.).

Results obtained for lines in the spectrum of Ba I.

Line.	Classification.	$\Delta \lambda$	$\Delta \nu$	Int.
5972 I.A.	${}^3P_2 - {}^3D_2$	{ +.137 0 -.062 -.129 }	{ -.384 0 +.173 +.362 }	{ 1 10 1 5 }
5536 "	Unclassified	{ +.044 0 -.041 -.065 }	{ -.144 0 +.133 +.212 }	{ 1 10 5 5 }
4934 "	Unclassified	{ +.043 0 -.037 }	{ -.175 0 +.152 }	{ 10 10 9 }
"	Unclassified	{ 0 -.060 }	{ 0 +.250 }	{ 10 2 }
4554 "	Unclassified	{ 0 -.051 -.085 }	{ 0 +.246 +.411 }	{ 10 9 8 }

TABLE IV.

Results obtained for lines in the spectrum of La II.

Line.	Classification.	$\Delta \lambda$.	$\Delta \nu$.	Int.
5304 I.A.	${}^3D_1 - {}^3D_2$	{ +.086 0 -.065 -.129 }	{ -.307 0 +.230 +.457 }	{ 2 10 4 4 }
5183 "	${}^3D_3 - {}^3D_3$		Single	
5123 "	${}^3D_2 - {}^3D_2$		Single	
5115 "	${}^3D_1 - {}^3D_1$		Single	

The intensities quoted above give merely the relative intensities of the components of a line.

It is not felt that the results given for the spectrum of lanthanum II are as satisfactory as those given for the spectra of the other elements. This spectrum possessing as it does a great number of lines is extremely difficult to investigate particularly with a highly resolving echelon spectrograph.

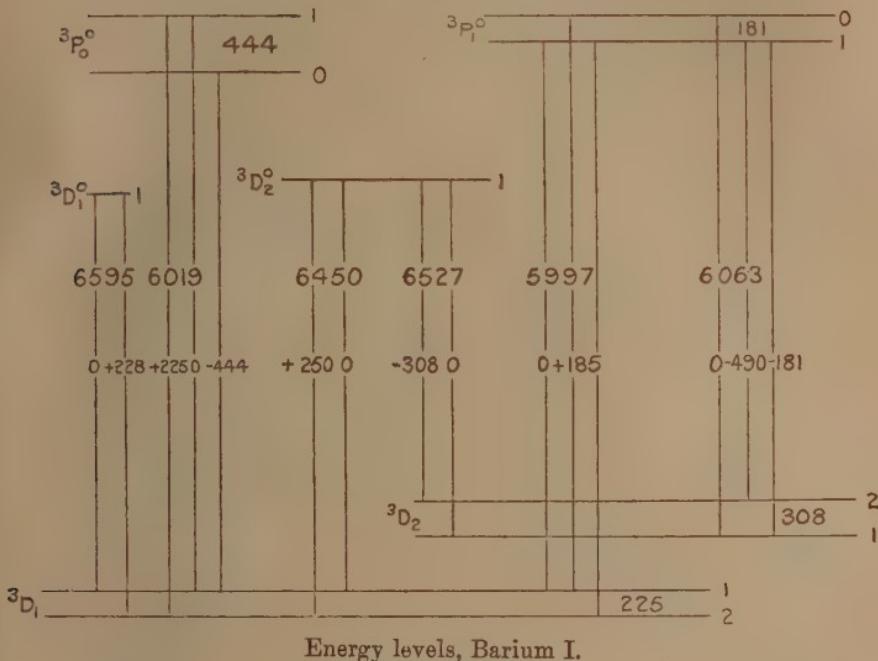
Plate I is from enlarged photographs of some of the lines that showed fine-structure. (a) shows the line 5304 of lanthanum, (b), (c), (d), (e), (f), (g) the lines 4554, 4934, 5536, 5972, 6063, 6595 respectively of barium and (h), (i) the lines 5378 and 6360 of cadmium.

The structures obtained for the lines in the arc spectrum of barium may be represented by the energy diagram given

in fig. 1. It is interesting to note that by assigning the quantum numbers indicated in the figure and applying the exclusion principles which are found to hold in the analysis of line spectra we obtain the number of components experimentally observed for these lines except in the case of the line 5997, which has one component missing.

Table V. has been drawn up to allow a comparison to be made between lines in the spectrum of Zn II. and lines in the spectrum of Cu I., between lines in the spectrum of Cd II. and lines in the spectrum of Ag I. and between lines in the spectrum of La II. and lines in the spectrum of Ba I.

Fig. 1.



Energy levels, Barium I.

TABLE V.

$^2P_2 - ^2D_3$	Single in Zn II.	Single in Cu I.
$^2P_1 - ^2P_2$	Single in Zn II.	Single in Cu I.
$^2P_1 - ^2D_3$	Doublet in Cd II.	Single in Ag I.
$^3D_1^0 - ^3D_2^0$	Quartet in La II.	Single in Ba I.
$^3D_3^0 - ^3D_2^0$	Single in La II.	Single in Ba I.
$^3D_2^0 - ^3D_2^0$	Single in La II.	Doublet in Ba I.
$^3D_1^0 - ^3D_1^0$	Single in La II.	Doublet in Ba I.

Using fig. 1 we may also compare the results obtained by us for the spectrum of Ba I. with those obtained by

Meggers and Burns for the spectrum of La II. They state that in La II, the level 3D_1 is triple at least, the level 3D_2 is single and the level 3D_3 is quintuple at least. We find that in Ba I, the level 3D_1 is double as is the level 3D_2 while the level 3D_3 appears single.

These results, as well as those previously published, lead to the conclusion that there is no similarity between the structure of a line in an arc spectrum and the structure of a line in the homologous series of the corresponding first spark spectrum. This is in keeping with the view advanced on theoretical grounds that the fine structure of a spectral line originates in a property—the spin—of the nuclei of the atoms giving rise to it.

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LIV. *On Weber's Law and Visual Acuity. By R. A. HOUSTOUN, D.Sc., Lecturer on Physical Optics in the University of Glasgow**.

THE power to distinguish differences in the brightness of objects is one of the most important properties of the human eye. It has hitherto been specified by the ratio $\Delta I/I$ where ΔI is the smallest increase in brightness which can be detected, when the eye is adapted to brightness I . This ratio has been measured by different observers during a period extending now over a century and a half, and Fechner stated that

$$\frac{\Delta I}{I} \text{ is constant.}$$

This result he called Weber's law. If we write ΔS to denote the increase in sensation,

$$\Delta S = k \frac{\Delta I}{I}.$$

This gives on integration $S = k \log I + C$, a result known as Fechner's law. It was obvious to Fechner that Weber's law did not hold for high and low intensities. But he considered that these deviations were due to disturbing factors, to dazzle at high intensities and to the intrinsic

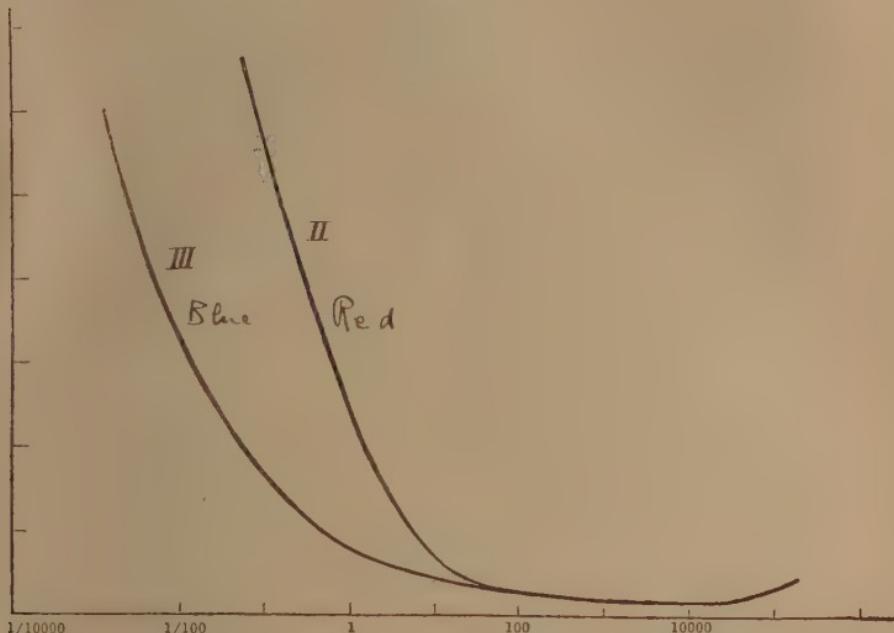
* Communicated by the Author.

light of the retina at low intensities, and regarded the ratio as constant for a wide interval between.

The most important investigation on the subject is that made by Koenig and Brodhun *, each of whom measured the ratio for white light and for six monochromatic regions of the spectrum over the whole range for which the eye can function.

Fig. 1 is a diagram representing their results taken from Helmholtz's 'Physiological Optics.' This diagram has now become classic. The ordinates represent the ratio. At high

Fig. 1.



intensities it is represented by the same curve I. for all colours, and at low intensities by the curve II. for the red end, and by the curve III. for the blue end of the spectrum.

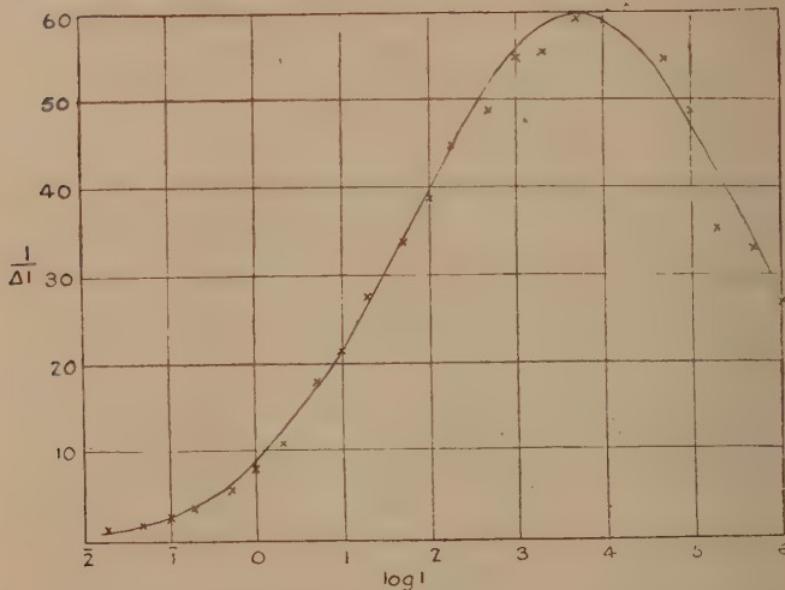
All the workers in the field have hitherto devoted their attention to the ratio $\Delta I/I$. In this it appears to me they have been wrong; it is not this quantity but its reciprocal that is important. What we are studying is the power of the eye to discriminate brightness; this should be measured by a number which is great when that power is great, and

* *Experimentelle Untersuchungen über die psychophysische Fundamentalformel in Bezug auf den Gesichtssinn. Sitzungsber. k. Akad. Wissensch. 1888, p. 917; 1889, p. 641.*

which should become zero, not infinite, in the case of a stone-blind man. I have consequently graphed in fig. 2 the mean of Koenig and Brodhun's values for $I/\Delta I$ for white light; the abscissæ are the logarithms of the intensity expressed in the arbitrary unit they used. The smooth curve is a probability curve $y=e^{-x^2}$ adjusted by trial and error to fit the data. A better fit might have been obtained by more elaborate methods, but the accuracy of the data hardly appears to warrant the extra trouble.

The fit is a good one. It shows that there can be no question of the validity of Fechner's law, that there is no

Fig. 2.



constant fractional increase, even for a limited interval. We are instead up against the laws of probability which always hold when there is a large number of objects grouped about a mean. In fig. 3 I have graphed the mean of Koenig and Brodhun's results for $605 \mu\mu$, and in fig. 4 the mean of their results for $470 \mu\mu$, in each case fitting a curve of the same type to the observations. In fig. 3 the fit is not so good as in fig. 2; the distribution is distinctly one-sided at the top. In fig. 4 there is a pronounced deviation at low intensities; it is this deviation that shows itself as the difference of the curves II. and III. in fig. 1.

Fig. 3.

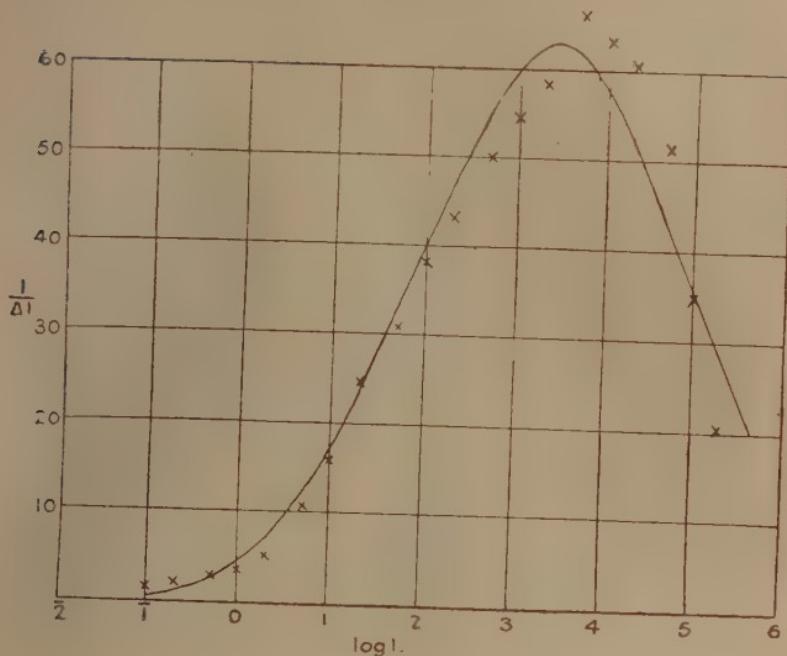
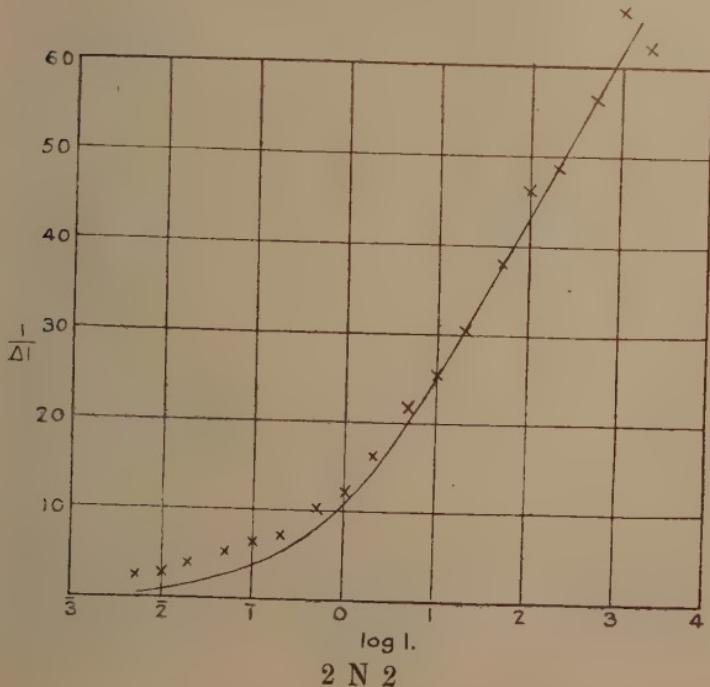


Fig. 4.



To convert the brightness of the surface to absolute units Koenig and Brodhun's should be multiplied by 0·04. It is then expressed in millilamberts; when a perfectly diffusing surface is exposed normally to a point source of one candle-power intensity at a distance of 1 cm., it has a brightness of 1 lambert. Koenig and Brodhun did not correct their intensities for the variation in the aperture of the pupil. Their numbers are proportional consequently to the intensity of the light outside the pupil not to its intensity on the retina, and should be corrected by multiplying by the area of the pupil opening. I have not made the correction as I am not sure of the value of the correction under the conditions of the experiment, and in any case it is not large enough to affect the shape of the curves appreciably. Koenig, it should be noted, had normal colour vision, whereas Brodhun was a dichromat, but there was no appreciable difference between their results. Ten settings were made by each observer at every intensity; it is doubtless impossible to increase the range over which the observations were made, but it is desirable that the work on white light should be repeated with a greater number of observations, in order to see how closely the results fit the probability curve.

The question arises as to why the variation takes place with regard to $\log I$, and not with regard to I ? I think it possible to answer this question with a fair degree of certainty. The percipient elements in the retina are the rods and cones or the cones alone. There are the two views. According to the duality theory the rods are a separate system from the cones functioning at lower intensities than the latter; this view is the more widely held at present. According to the other view the rods are not percipient elements. On the first view the rods and cones are connected to the fibres of the optic nerve. Now we know as a consequence of the work of Adrian that the sensation is propagated along the nerve fibre by a series of impulses. The velocity of the impulses is constant, but their frequency increases with the intensity of the stimulus. R. S. Lillie has described a model which imitates very closely the propagation of the pulses. If an iron wire is dipped into a strong solution of nitric acid, its surface becomes "passive," *i.e.*, becomes covered by a sheath of oxide which protects it from the further action of the acid. If the wire is then immersed in a weaker solution of the acid and its surface touched with a zinc rod, the sheath is destroyed at the point of contact, and a pulse characterized by effervescence travels

rapidly along the wire. The sheath reforms behind the pulse, and after a short interval of time the wire is in a condition to transmit another pulse. By analogy the impulse in the fibre of the optic nerve should be started by applying a charge of electricity to the surface of the cone.

The light falls first on a photosensitive substance liberating electrons. These pass through an absorbing medium to the surface of the cone. Now a stream of electrons is absorbed according to the same law as a ray of light. If I denotes the initial and I_0 the final intensity of the stream,

$$I_0 = I e^{-\mu x}$$

where μ is a constant and x denotes the length of the path in the medium. Consequently

$$\log I_0 = \log I - \mu x.$$

The length of the path will vary from cone to cone. One value will be most common and the others will be distributed around this. If we divide the cones into classes according to the value of x which they possess, and graph the number in each class against the value of x , we obtain a frequency distribution. Let us assume that the same intensity I_0 is required to start an impulse in each cone, then according to the above equation the distribution has the same shape, when it is graphed against $\log I$ instead of x .

When $\log I$ is small, all the cones are inactive. If $\log I$ is increased, each cone becomes active as its threshold is reached. Let us assume, that for a just perceptible increase in sensation the number of active cones always increases by the same amount. Then the ordinates in figs. 2, 3, and 4 represent the rate of increase of the number of active cones with the increase in $\log I$ where I denotes the intensity of the stream of electrons. Let us take the latter as proportional to the intensity of the incident light. The figs. then represent the distribution of the cones or other percipient elements in terms of the logarithms of their threshold intensities.

The photo-sensitive substance decomposes under the incident light and recombines again in the dark. The intensity of the stream of electrons is proportional to the incident light only if the quantity of substance decomposed is small. It is possible that there may be an effect due to the exhaustion of the photosensitive substance. Also, when a cone becomes active, its rate of activity increases with the increase in the intensity of the light until a stationary condition is reached, determined by the interval

necessary for the nerve to recover from the passage of the previous impulse. This stationary condition must, however, be reached very rapidly, otherwise the curves in figs. 2 and 3 would have no descending portions. Probably a satisfactory approximation to actual conditions will be obtained if we assume that all cones function at the same intensity once they are started, and if we place the threshold for each cone midway between its actual value and the intensity which produces the stationary condition. But the curves make it practically certain that the main consideration is a probability one which can be nothing else but the grouping of the percipient elements round a particular threshold intensity.

The question arises as to the nature of the percipient elements. According to the view most prevalent at present, the rods should function at low intensities, and there should be three different kinds of cones corresponding to the fundamental sensations of the Young-Helmholtz theory of colour vision. In fig. 2 I can see evidence only for one mechanism. In fig. 3 the one-sided distribution may be due to the overlapping of symmetrical distributions due to the different fundamental sensations of the Young-Helmholtz theory. It is, however, well to remember that most distributions which occur in nature due to the variation of one factor are one-sided; the Gaussian distribution is the exception rather than the rule. The deviation in fig. 4 may be due to a second system, presumably the rods; or it may be due to spherical aberration of the eye for blue light. We are compelled to suspend judgment, for there is not enough to form judgment upon.

According to the assumption of this paper, the sensation is proportional to the number of active percipient elements. If S denotes the sensation and the curve in fig. 2 is accurately represented by the probability expression, it follows that

$$\frac{dS}{d(\log I)} = k e^{-\frac{(\log I - \log I')^2}{2\sigma^2}}$$

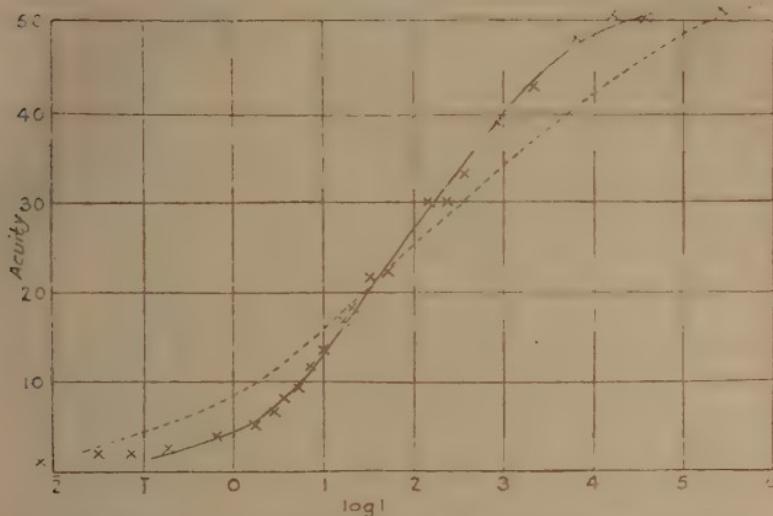
where I' is the intensity at the maximum and σ is the "dispersion" or standard deviation. Hence we have

$$S = k \int_{-\infty}^x e^{-\frac{(\log I - \log I')^2}{2\sigma^2}} d(\log I)$$

instead of Fechner's law $S = k \log I + C$. This is an integral widely used in statistical work, and there are tables giving its value.

In 1897 Koenig* measured the resolving power of the eye for white, red, green, and blue light over as wide a range of intensities as possible. He used Snellen's test object **W** upon a background of the colour in question; this is turned left or right or up or down, and the measurement consists in finding at what intensity the direction of the open side can just be determined. If this can be done when the object subtends an angle of 5 minutes at the eye, the resolving power or acuity is said to have unit value. If the direction can be determined when the angle subtended is $2\frac{1}{2}$ minutes, the resolving power is 2. His results for white light are represented by the crosses in fig. 5 on the same

Fig. 5.



scale of intensity used for figs. 2, 3, and 4. The ordinates give acuity. The intensity is not corrected for variations in the aperture of the pupil. Koenig's observations were rather numerous, and have been averaged in groups of five consecutive readings by Hecht†; it is Hecht's averages that are represented in the fig. I have fitted a curve of the type

$$y = \int_{-\infty}^x e^{-z^2/2} dz$$

to the observations adjusting the origin and scale by trial and error. The agreement is within the experimental error.

* *Die Abhängigkeit der Sehschärfe von der Beleuchtungsintensität.* *Sitzungsber. k. Akad. Wissensch.* 1897, p. 559.

† "The Relation between Visual Acuity and Illumination." *J. Gen. Physiol.* 1928, xi. p. 255.

It will be noted that this curve is of the same type as has been used to represent S , and that there are no signs of two mechanisms.

On what should the variation of acuity with intensity depend? According to Hecht it depends only on the number of active percipient elements in unit area of the retina. The number of percipient elements is fixed anatomically. Hence we must assume that more become active as the intensity is increased, that is, we make the same assumption as before, namely, that the elements have different intensity thresholds. Let us suppose they are arranged in rows at equal distances from one another, and that there are N per cm. The number per unit area is consequently N^2 , and this is proportional to S . The acuity as defined above is presumably inversely proportional to the distance between two percipient elements, *i.e.*, it is proportional to N . It is hence proportional to \sqrt{S} . I have calculated S from Brodhun's measurements on white light, and have plotted \sqrt{S} as a broken line in fig. 5, choosing the scale of ordinates to give as good an agreement as possible. But \sqrt{S} cannot be said to fit the observations, although the change takes place over the same range.

A little consideration shows that Hecht's assumption requires to be modified. If we consider the analogy with the photographic plate, the detail in the image certainly increases as the distance between the grains decreases. But it depends also on the degree of contrast in the plate. A plate with soft gradation which fogs slightly in the developer does not show up detail as well as a clean working plate. Something similar must happen in the retina. Let us suppose that the test object consists of two thin parallel white strips separated by a thin black strip. The black strip is not perfectly black, and we shall suppose that it reflects one-twentieth as much light as the white strip does. At low intensities the light reflected from the black strip is below the thresholds of all the percipient elements. As the intensity is raised, the light reflected from the black strip rises above the threshold of element after element; finally, when the intensity is very great, the light from the black strip is above the threshold of most of the elements. The degree of contrast consequently varies with the intensity of illumination. To obtain the acuity from \sqrt{S} we must multiply the latter by a contrast factor. But the excellent agreement of the observations with the probability curve makes it certain that number of elements and contrast

should not be considered separately ; the variation must depend on a single factor involving both these quantities.

It would be well in future determinations of the resolving power of the eye to use a series of equidistant parallel lines as test object, so as to eliminate disturbance due to end effects. Such a test object as Snellen's has the advantage that it eliminates dishonest work, and is valuable when examinations in visual acuity are a condition of admission to trades and professions. But in a scientific investigation the object should be geometrically as simple as possible.

Koenig found that the acuity was independent of the colour of the light. The readings for red, green, and blue agreed with the readings for white light, whenever the intensities were reduced to the same unit.

If the percipient elements reach their thresholds gradually as the intensity increases, the question may be asked, why, when we look at a white sheet, does the image not show a grain at low intensities. It is possible that the brain interprets a particular kind of graininess as uniform intensity, just as it recognizes an inverted image on the retina as that of an erect walking man. But it is more probable that the threshold of each element changes frequently, as the supply of photosensitive substance varies, and that the uniformity is due to persistence of vision.

In order to explain the increase in sensation with intensity it might be suggested that the cones have all the same threshold, but that the molecules of the photosensitive substance have different thresholds, *i.e.*, some are decomposed more readily than others. But this will not explain the variation of acuity with intensity.

In measuring the resolving power of the eye for blue light, Koenig found that it increased more rapidly than it ought to increase, when he approached the the test object. Careful correction of the eye for myopia in the blue had no effect, and he concluded that the discrepancy was due to a large spherical aberration of the eye for blue light. He offers no explanation of the difference between curves II. and III. in fig. 1. It is possible that this is due to the same cause, for spherical aberration would blur the dividing edge of the comparison fields, and render the arrangement less sensitive. It would naturally come into play at low intensities when the full pupil was used.

In order to see how closely the results fit the probability curve and settle some of the other points raised in this paper, we are at present preparing to repeat Koenig and Brodhun's entire investigation

LV. *The Effect of Boundary Distortion on the Surface Energy of a Crystal.* By BERYL M. DENT, Department of Theoretical Physics, Bristol University*.

§ 1. INTRODUCTION.

AS there is as yet no reliable experimental method of determining the surface energies of solids, and as a knowledge of the magnitude of the surface energy is essential to a proper understanding of many surface phenomena, any theoretical estimate of this quantity is of interest.

Hitherto it has only been possible to calculate the surface energy † on the assumption that the effect of the distortion or shrinking of the boundary of the crystal can be neglected, for the simple reason that no method existed of estimating the extent of this distortion. This has now been done. It has been shown ‡ that for a series of alkaline halide crystals it is the deformability of the surface ions which largely controls the distortion at the surface. If the ions were not deformable, the distortion would practically vanish. Actually the contraction in the interplanar spacing at the surface is about five per cent., and reasons have been given for supposing that this contraction is practically confined to the topmost layer.

The surface energy is found to be similarly sensitive to the deformability of the surface ions. Calculations for eight crystals of the rock-salt type show that the surface energy of the (100) plane is diminished by about 20 per cent., due to the deformability of the surface ions and the consequent contraction at the surface.

§ 2. METHOD.

In Born's notation § let the potential energy of the unbroken crystal be divided into three parts,

$$\phi = \phi_{11} + \phi_{22} + \phi_{12},$$

where ϕ_{11} and ϕ_{22} are the energies of the two parts which are separated by the net plane along which the crystal is broken, and ϕ_{12} is the mutual energy of these two parts.

* Communicated by Professor J. E. Lennard-Jones.

† Born, 'Atomtheorie des festen Zustandes,' 2nd ed., p. 538; Lennard-Jones and Taylor, Proc. Roy. Soc. cix. p. 476 (1925).

‡ Lennard-Jones and Dent, Proc. Roy. Soc. cxxi. p. 247 (1928).

§ Born, *loc. cit.*

The energy zero is assumed to correspond to a state of infinite dispersion of the ions, hence all the ϕ 's are negative.

As the two parts of the crystal are separated, the two freshly-formed bounding surfaces will be slightly deformed, so that the energies ϕ_{11}^* and ϕ_{22}^* , after breaking, will be different from ϕ_{11} and ϕ_{22} respectively. The total energy after breaking

$$= \phi^* = \phi_{11}^* + \phi_{22}^*.$$

The surface energy σ is defined by the equation

$$\sigma = \frac{1}{2F} (\phi^* - \phi), \quad \dots \quad (2.1)$$

where F is the area of each new surface.

Hence

$$\sigma = \frac{1}{2F} \left\{ -\phi_{12} + (\phi_{11}^* - \phi_{11}) + (\phi_{22}^* - \phi_{22}) \right\}.$$

We suppose that the two parts are identical, so that

$$\phi_{11} = \phi_{22}; \quad \phi_{11}^* = \phi_{22}^*,$$

$$\text{and therefore } \sigma = -\frac{\phi_{12}}{2F} + \frac{\phi_{11}^* - \phi_{11}}{F}. \quad \dots \quad (2.2)$$

Usually the difference $\phi_{11}^* - \phi_{11}$ is neglected, but we are now in a position to evaluate it.

$$\text{Let } \sigma' = -\phi_{12}/2F, \quad \dots \quad (2.3)$$

$$\text{and } \sigma'' = (\phi_{11}^* - \phi_{11})/F. \quad \dots \quad (2.4)$$

$$\text{Then } \sigma = \sigma' + \sigma''. \quad \dots \quad (2.5)$$

Since ϕ_{12} is negative, σ' is positive. σ'' , on the other hand, is negative because the energy tends to a minimum, and therefore $\phi_{11}^* < \phi_{11}$. Hence the effect of shrinking at the boundary is to decrease the surface energy.

§ 3. CALCULATION OF σ' .

In order to calculate σ' a knowledge of the repulsive forces between the different ions occurring in the crystals is necessary. These repulsive forces have been investigated by Lennard-Jones in a series of papers on the assumption that they may be expressed by an inverse power law (λ/r^n), and a table of the repulsive force constants (λ) and indices (n) for many monovalent and divalent ions is given in the last of these papers †.

† Lennard-Jones and Dent, Proc. Roy. Soc. exii. p. 230 (1926).

A method of calculating σ' has already been published, and numerical results have been obtained for four of the crystals dealt with in this paper, viz., NaF, NaCl, KF, KCl†. These values have been recalculated, using the slightly improved values of the force constants given in the table mentioned above, and the calculations for the remaining four crystals have been carried out. The results are given in Table I.‡ The units are ergs per square cm.

TABLE I.

Values of σ' (Surface Energy, neglecting boundary distortion).

	F.	Cl.	Br.	I.
Na	307	93	90	88
K	178	75	73	72

§ 4. CALCULATION OF σ'' .

From equation (2.4)

$$\sigma'' = (\phi_{11}^* - \phi_{11})/F,$$

where ϕ_{11} is the energy of the semi-infinite crystal bounded by a (100) plane, and ϕ_{11}^* is the energy of the same crystal after breaking. Now it has been shown that the shrinking at the surface is practically confined to the top layer, and therefore the difference between ϕ_{11}^* and ϕ_{11} is mainly due to the ions in the surface layer. We therefore calculate the potential energy of a pair of unlike ions in the bounding plane, firstly in their original positions in the unbroken crystal, and, secondly, in their distorted positions. Let these energies be ϕ_s and ϕ_s^* respectively. Then

$$\phi_{11}^* - \phi_{11} = \phi_s^* - \phi_s, \text{ approx.},$$

and $\sigma'' = (\phi_s^* - \phi_s)/F, \text{ approx. . } (4.01)$

† Lennard-Jones and Taylor, *loc. cit.* p. 496.

‡ The calculations involve the size of the unit cell of each crystal. This quantity can be calculated by means of the force constants and indices mentioned above, and the results are found to agree very closely with those observed. See Proc. Roy. Soc. *xxxi*. p. 253, Table 4 (1928). For the sake of consistency, the calculated values have been used throughout.

(i.) Calculation of ϕ_s .

ϕ_s is made up of two parts, viz., ϕ_{s^e} , the energy due to electrostatic forces, and ϕ_{s^r} , the energy due to repulsive forces. We may neglect that due to polarization before the crystal is broken, since, in the interior of a crystal of symmetrical pattern, any displacement of the nucleus of an ion relative to the centre of the electronic structure is improbable. We also neglect the contribution of van der Waals's forces—this is negligible compared with the electrostatic potential. We therefore have

$$\phi_s = \phi_{s^e} + \phi_{s^r}. \quad (4.02)$$

In the notation of a former paper †

$$\phi_{s^e} = -\frac{8e^2}{a} \sum'_{l,m} (l^2 + m^2)^{-\frac{1}{2}} c_{l,m} f_{l,m}(z) + A(a/2), \quad (4.03)$$

where $A(a/2)$ represents the effect of the remaining ions in the surface plane and is independent of z (the distance between the surface and the second plane), and the first term represents the effect of the rest of the crystal. The interatomic distance in the surface plane itself ($a/2$) is assumed to remain unaltered after breaking, and therefore the same quantity A will appear in the electrostatic potential energy $\phi_{s^e}^{*e}$. A similar quantity B will appear in the expressions for ϕ_{s^r} and $\phi_{s^r}^{*r}$. Both A and B will disappear on subtraction (see equation 4.01), and will be omitted in future.

It is convenient to write

$$\phi_{s^e} = -\frac{32e^2}{a} s_3(z/a), \quad (4.04)$$

where

$$s_3(z/a) = \frac{1}{4} \sum'_{l,m} (l^2 + m^2)^{-\frac{1}{2}} c_{l,m} f_{l,m}(z), . . . \quad (4.05)$$

in conformity with the notation of a recent paper ‡, where

$$s_1(z/a) = \frac{1}{4} \sum'_{l,m} c_{l,m} f_{l,m}(z)$$

and

$$s_2(z/a) = \frac{1}{4} \sum'_{l,m} (l^2 + m^2)^{\frac{1}{2}} c_{l,m} f_{l,m}(z).$$

† Lennard-Jones and Dent, Trans. Faraday Soc. xxiv. p. 92 (1928).

‡ Lennard-Jones and Dent, Proc. Roy. Soc. cxxi. p. 250 (1928).

In the undistorted case $z/a = 0.5$ and $s_3(z/a) = 0.825 \cdot 10^{-2}$ (see Table IV.). The values of ϕ_s^r for the eight crystals are given in Table III. The contribution of the repulsive forces to the potential is easily seen to be

$$\begin{aligned} \phi_s^r = & \frac{2\lambda_{12}k'(n_{12}, z/a)}{(n_{12}-1)(a/2)^{n_{12}-1}} + \frac{\lambda_{11}k''(n_{11}, z/a)}{(n_{11}-1)(a/2)^{n_{11}-1}} \\ & + \frac{\lambda_{22}k''(n_{22}, z/a)}{(n_{22}-1)(a/2)^{n_{22}-1}}, \quad . \quad (4.06) \end{aligned}$$

where $\lambda_{12}/r^{n_{12}}$, $\lambda_{11}/r^{n_{11}}$, and $\lambda_{22}/r^{n_{22}}$ are the laws of force between a positive and a negative ion, between two positive, and between two negative ions respectively, and

$$\left. \begin{aligned} k'(s, z/a) = & \sum_{\substack{n \neq 0 \\ l+m+n \text{ even}}} \{l^2 + m^2 + (2z/a + n)^2\}^{-(s-1)/2} \\ k''(s, z/a) = & \sum_{\substack{n \neq 0 \\ l+m+n \text{ odd}}} \{l^2 + m^2 + (2z/a + n)^2\}^{-(s-1)/2} \end{aligned} \right\}. \quad (4.07)$$

A method of evaluating these summations has already been given *. It consists in calculating by direct summation the contribution of the ions within a certain spherical cap and in replacing the rest by a continuum, each volume element of which repels or attracts according to the appropriate law. The height of the spherical cap was taken to be $3a/2$ in each case.

Values of k' and k'' for $s = 9, 10, 11$, and for two typical values of $z/a = 0.42$ and 0.50 are given in Table II. †

TABLE II.

s .	k' .			k'' .		
	9.	10.	11.	9.	10.	11.
$z/a = 0.42$	4.133	4.858	5.750	0.4966	0.3725	0.2820
$z/a = 0.50$	1.065	1.035	1.019	0.2663	0.1834	0.1278

* Lennard-Jones and Dent, Trans. Faraday Soc. loc. cit.

† I should like to thank Mr. F. E. L. Parsons, The University, Bristol, for his help in calculating a series of these summations.

Values of ϕ_s^r are given in Table III.

TABLE III.

Potential Energy of a Pair of Unlike Ions in the Undistorted Surface.

Crystal.	NaF.	NaCl.	NaBr.	NaI.	KF.	KCl.	KBr.	KI.
$\phi_s \cdot 10^{12}$ ergs...	-1.310	-1.053	-1.010	-0.945	-1.137	-0.962	-0.928	-0.868
ϕ_s^r .. .	+0.637	+0.716	+0.661	+0.564	+0.612	+0.639	+0.599	+0.501
ϕ_s .. .	-0.673	-0.337	-0.349	-0.381	-0.525	-0.323	-0.329	-0.367

(ii.) Calculation of ϕ_s^* .

The potential energy of a pair of ions in the distorted surface is made up of three parts :

$$\phi_s^* = \phi_s^{*e} + \phi_s^{*r} + \phi_s^{*p}, \dots \quad (4.08)$$

where ϕ_s^{*p} is the energy due to the polarization of the surface ions.

The calculation of ϕ_s^{*e} and ϕ_s^{*r} is exactly similar to that of ϕ_s^e and ϕ_s^r , except that z/a , instead of being 0.5, must be given its appropriate value for each crystal, i.e., the equilibrium distance between the two outermost layers. These values of z/a have been calculated in a previous paper †, and are reproduced in Table VI. (as $(z/a)_0$).

We require the values of the summations $s_3(z/a)$, $k'(s, z/a)$, and $k''(s, z/a)$ for these equilibrium values of z/a . These were all obtained by graphical interpolation of a series of calculated values. Values of s_3 are given in Table IV.

TABLE IV.
Values of Certain Summations. . .

z/a	0.42	0.45	0.46	0.48	0.49	0.50
$s_1 \cdot 10^2$	2.416	1.840	1.681	1.403	1.282	1.172
$s_3 \cdot 10^2$	1.689	1.290	1.180	0.987	0.902	0.825

The values of ϕ_s^{*e} and ϕ_s^{*r} are given in Table VI.

† Lennard-Jones and Dent, Proc. Roy. Soc. cxxi. p. 247 (1928) (see Table VI.).

In order to calculate the effect of the polarizability of the ions, we assume, as usual, that in an electric field a dipole is produced in each ion whose strength is proportional to the field. The moment of the induced dipole is then

$$p = \alpha E,$$

where E is the electric field and α is an atomic constant called the coefficient of polarizability. This assumption is used in the theory of dielectrics, and, while it is probably justified for a weak homogeneous field, it is only a first approximation for an ion in the rapidly fluctuating field at the surface of a polar crystal. The electric field at any ion is due partly to the electrostatic charges in the remainder of the crystal and partly to the field set up by the array of dipoles in the surface. In the notation of a previous paper * we write the fields at a positive and negative ion respectively as

$$\left. \begin{aligned} E_1 &= E_1^o + E_1^d = \eta_1 E_1 \\ E_2 &= E_2^o + E_2^d = \eta_2 E_2^o \end{aligned} \right\}, \quad \dots \quad (4.09)$$

where η_1 and η_2 are functions of the coefficients of polarizability and the size of the unit cell. Values of η_1 and η_2 for the eight crystals here considered are given in Table V. The values of α , the coefficient of polarizability, were taken from a paper by Born and Heisenberg †.

TABLE V.

Values of η_1 and η_2

Crystal.	NaF.	NaCl.	NaBr.	NaI.	KF.	KCl.	KBr.	KI.
η_1	1.35	1.54	1.61	1.71	1.17	1.41	1.51	1.60
η_2	0.902	0.762	0.715	0.658	1.13	0.936	0.880	0.807

The potential energy of a dipole in an electric field is easily shown to be $-\frac{1}{2}\alpha E^2$, and therefore the potential energy of the two dipoles induced in a pair of unlike ions ‡

* *Ibid.* § 2.

† *Z. f. Physik*, xxiii, p. 388 (1924).

‡ Since the potential energy of a dipole at a point on a line bisecting it at right angles is zero, the presence of the dipoles will not affect the potential field at any point in the surface, and will, therefore, make no difference to the term ϕ_s^{*e} . The energy due to the dipoles is, therefore, completely accounted for by the term ϕ_s^{*p} .

$$\begin{aligned}
 -\phi_s^{*p} &= -\frac{1}{2}\alpha_1 E_1^2 - \frac{1}{2}\alpha_2 E_2^2 \\
 &= -\frac{1}{2}\alpha_1 \eta_1^2 (E_1^c)^2 - \frac{1}{2}\alpha_2 \eta_2^2 (E_2^c)^2 \\
 &= -\frac{1}{2}(E_1^c)^2 \{\alpha_1 \eta_1^2 + \alpha_2 \eta_2^2\}, \dots \quad (4.10)
 \end{aligned}$$

since $E_1^c = -E_2^c$.

Now †

$$E_1^c = -(32\pi e/a^2)s_1(z/a). \dots \quad (4.11)$$

The necessary values of the summation s_1 were found by graphical interpolation of the calculated values given in Table IV. Values of ϕ_s^{*p} are given in Table VI. For reasons given above (p. 536), no great accuracy is claimed for these values. They must be regarded as rough estimates only.

TABLE VI.

Potential Energy of a Pair of Unlike Ions
in the Distorted Surface.

Crystal.	NaF.	NaCl.	NaBr.	NaI.	KF.	KCl.	KBr.	KI.
$(z/a)_0$	0.483	0.475	0.469	0.472	0.476	0.465	0.460	0.469
$\phi_s^{*e} 10^{12}$ ergs...	-1.527	-1.316	-1.331	-1.213	-1.405	-1.311	-1.330	-1.148
ϕ_s^{*p} ..	-0.057	-0.053	-0.058	-0.053	-0.076	-0.085	-0.096	-0.076
ϕ_s^{*r} ..	+0.866	+1.005	+1.015	+0.866	+0.915	+1.036	+1.058	+0.824
ϕ_s^* ..	-0.718	-0.364	-0.374	-0.400	-0.566	-0.360	-0.368	-0.400

From equation (4.01) we have

$$\sigma'' = (\phi_s^* - \phi_s)/F,$$

where F is the area of a cell containing two unlike ions and $= \frac{1}{2}a^2$, $a/2$ being the smallest distance between the two ions. Values of σ'' are given in the second row of Table VII. The units are ergs per square cm.

§ 5. RESULTS.

The total surface energy is given by $\sigma = \sigma' + \sigma''$ (equation 2.5), and is to be found in Table VII. The surface energy due to distortion is also given as a percentage correction to σ' .

† Lennard-Jones and Dent, Proc. Roy. Soc. cxxi. p. 250 (1928).

TABLE VII.

Surface Energy of Certain Salts (100 plane).

Crystal.	NaF.	NaCl.	NaBr.	NaI.	KF.	KCl.	KBr.	KI.
σ' ergs/cm. ² ...	+307	+93	+90	+88	+178	+75	+73	+72
σ'' ,,	- 42	- 16	- 14	- 9	- 29	- 19	- 19	- 14
σ ,,	+265	+77	+76	+79	+149	+56	+54	+58
Percent. Corr.								
σ''	14	17	16	10	16	25	26	19
σ'								

It is sometimes useful to express the surface energy per pair of unlike ions, instead of per unit area. If ρ is the total surface energy per pair of unlike ions, then $\rho = \rho' + \rho''$, where $\rho' = -\phi_{12}/2$ and $\rho'' = \phi_{11}^* - \phi_{11} = \phi_s^* - \phi_s$. Values of ρ' , ρ'' , and ρ are given in Table VIII.

TABLE VIII.

Surface Energy per Pair of Unlike Ions.

Crystal.	NaF.	NaCl.	NaBr.	NaI.	KF.	KCl.	KBr.	KI.
$\rho' 10^{12}$ ergs...	+0.325	+0.152	+0.161	+0.179	+0.250	+0.147	+0.153	+0.175
ρ'' ,,	-0.045	-0.027	-0.025	-0.019	-0.041	-0.037	-0.039	-0.038
ρ ,,	+0.280	+0.125	+0.136	+0.160	+0.209	+0.110	+0.114	+0.142

It is seen (Table VII.) that the correction due to distortion at the surface varies from 10 to 26 per cent.* This correction has hitherto been assumed negligible, but it now appears that the assumption is not justified. An accurate determination of the surface energy of an ionic crystal must take the distortion at the surface into account.

* Biemuller (*Z. f. Physik*, xxxviii. p. 759, 196) has investigated the effect of the polarizability of the ions on the surface energy of several alkaline halide crystals (100 and 110 planes). He assumes, however, that the positions of the ions in the surface are unchanged, which is contrary to the result obtained by Lennard-Jones and Dent, Proc. Roy. Soc. cxxi. p. 247 (1928).

§6. SUMMARY.

1. A method of evaluating the effect of surface distortion on the surface energy of polar crystals is described.

2. The results for eight monovalent alkaline halides are given, and show that the distortion decreases the surface energy by about 20 per cent.

3. The effect is found to be due almost entirely to the polarization of the surface ions.

My thanks are due to Professor J. E. Lennard-Jones for suggesting this problem to me, and for his interest in the work.

LVI. *The Interpretation of the Temperature Coefficient of Surface Tension.* By N. K. ADAM, M.A., Sc.D. (Royal Society Sorby Research Fellow) *.

THE object of this paper is to suggest some kinetic considerations, which, although far from rigorous, indicate that many properties of the molecules of liquids, besides molecular association, must affect the value of the differential coefficient of the "molecular free surface energy"

$$k = - \frac{d}{dT} \left\{ \gamma (Mv)^{2/3} \right\} \dots \dots \quad (1)$$

γ being the surface tension and Mv the molecular volume; k is often called the "Eötvös" constant. A few new data on the surface tension of long chain compounds are also presented.

Hunten and Maass † have recently considered the temperature coefficient of surface tension, and related functions, in the case of homologous series of aliphatic compounds. They point out that orientation of the surface molecules perpendicular to the surface will increase the number of molecules in the surface, and so the value of k . This paper suggests a new way of regarding the temperature coefficient, and shows that numerous other properties of the molecules, most of which cannot be allowed for in the present state of kinetic theory, will probably affect the value of k .

The inadequacy of the original theory of Eötvös ‡ and Ramsay and Shields §, as a means of determining the degree

* Communicated by the Author.

† J. Amer. Chem. Soc. p. 153 (1929).

‡ Wied. Ann. xxvii. p. 448 (1886).

§ Phil. Trans., A, p. 647 (1893).

of association in liquids, is now fairly generally recognized ; they claimed that k has a value close to 2·1 for all liquids, if M is taken as the actual molecular weight of the liquid allowing for association. Jaeger's results* illustrate the enormous variations found in k , when a sufficiently extended range of compounds is taken ; thus he found values from 0·67 up to 6·75 for ordinary organic liquids, k being not always constant even for a single substance. For liquid crystals the variations in k are much greater even than this.

It appears that the Eötvös constant k actually varies more than does the simple temperature coefficient of surface tension, $-\frac{d\gamma}{dT}$, for organic substances. In a table of over

three hundred organic compounds, Harkins, Davies, and Clark † give no values greater than 0·18 or less than 0·05. Experience also shows that the value of k (see Hunten and Maass) rises steadily with the molecular weight, so that it appears that the plan of multiplying by a function of the molecular weight has not been altogether successful in bringing the physical quantity, $-\frac{d\gamma}{dT}$, to a common basis for different substances.

Ramsay and Shields stressed the analogy between the rise in surface tension as the temperature falls from the critical, and the rise in gaseous pressure as the temperature of a gas rises. The mechanism underlying this analogy is not easily seen in this statement, as the quantities considered move in opposite directions with temperature ; and surface tension is not a tangible physical quantity in terms of molecules, like gaseous pressure, but is only the mathematical equivalent of free surface energy.

By considering the effect of the bombardment of a barrier in the surface by the molecules of the liquid, some idea may be obtained of the meaning of the temperature coefficient of surface tension. If a barrier separates two regions at different temperatures, the bombardment on the warm side of the barrier will be more intense than that on the cold side. Let the lateral pressure due to this bombardment be F and $F+dF$, at temperatures T and $T+dT$. The net lateral pressure per centimetre in the surface will be dF dynes, away from the warm side.

Suppose that this barrier is affected only by the molecules in the surface layer, which we will assume is n molecules.

* Z. anorg. Chem. ci. p. 1 (1917).

† J. Amer. Chem. Soc. p. 556 (1917).

thick. It is thus purely ideal, as no barrier can be conceived which distinguishes between the molecules in the surface and those in the interior; nevertheless it enables calculations to be made which may illustrate the effect of the molecular motions. The net force on this barrier, dF , is clearly equal to the decrease in surface tension, $-d\gamma$, with the rise in temperature dT , for if the barrier is moved through a distance dx , the work done may be written either as dF/dx , or as $-d\gamma/dx$.

With most substances, the decrease in surface tension is nearly linear as the temperature rises; therefore F , the lateral bombardment pressure, increases linearly with temperature. This is strictly analogous to the linear rise of the pressure of a gas, with rising temperature, and is due to the same cause, namely, the increased intensity of bombardment of the boundaries by the molecules; thus if we focus attention on the thermal pressure in the liquid surface, instead of on the surface tension, the comparison between the liquid and the gas is seen to be very close.

Factors Determining the "Eötvös Constant" on the preceding Theory.

The Eötvös constant (1) becomes

$$k = \frac{d}{dT} \left\{ F(Mv)^{2/3} \right\} \dots \dots \quad (3)$$

If the molecules are symmetrical and may be taken as occupying cubical space, the number N_0 per square centimetre is

$$n \left(\frac{N}{Mv} \right)^{2/3},$$

where N is the Avogadro number, and n the thickness of the surface layer in molecules.

(3) then becomes

$$\frac{d}{dT} \left(\frac{F}{N_0} \right) = \frac{k}{n N^{2/3}} = 1.395 \times 10^{-16} \frac{k}{n} \dots \dots \quad (4)$$

But if A is the area per molecule, $\frac{F}{N_0} = FA$,

and (4) is of the same form as the equation

$$\frac{d}{dT} (FA) = R = 1.372 \times 10^{-16} \dots \dots \quad (5)$$

obtained if we differentiate the equation of state of a two-dimensional gas, $FA = RT$.

It is interesting to compare the value of k with that which would be obtained, on the above theory, if the rate of variation of the horizontal bombardment pressure F with temperature were actually the same as that of a perfect gas. If this is the case, comparison of (4) and (5) shows that

$$k=0.985n \dots \dots \dots \quad (6)$$

It may be more than a coincidence that this value of k is of the same order of magnitude as the experimentally determined values; n , the number of molecules in the thickness of the surface layer, is certainly small.

Association of the molecules will on this theory cause k to vary inversely as the two-thirds power of the degree of association, as in Ramsay and Shields' theory, by diminishing the number of separate molecules in the surface layer in this ratio. Elongation of the molecules, and orientation perpendicular to the surface, will increase the number in the surface, and therefore increase k . If the molecules are x -times as long as thick, then the number in the surface is

$$nx^{2/3} \left(\frac{N}{Mv} \right)^{2/3}$$

and the constant is increased in the ratio $x^{2/3}$. Thus molecules eight times as long as thick, if oriented perpendicular to the surface, will increase k four times.

It thus appears that the orientation of the molecules, if elongated, and the thickness of the surface layer, as well as simple molecular association, will affect the value of the Eötvös constant k . And perhaps more important still are the factors which may make the comparison between (4) and (5) invalid, by rendering the rate of increase of the thermal pressure in a horizontal direction, in the liquid, different from the rate of increase of gaseous pressure with temperature; these may include the chemical attractions laterally between the molecules, and details of their shape also.

Further developments are only likely to follow when the kinetic theory of liquids is more fully understood; but these considerations are advanced as showing perhaps which properties of surfaces may be useful in developing the kinetic theory of liquids by comparison with experiment. Born and Courant's discussion * of the theory of liquid surfaces gave a value of about 2.1 for k , when the number of degrees of freedom of the surface molecules was taken as

* *Physikal. Z.* xiv. p. 731 (1913).

three ; if the number of degrees of freedom had been n , the constant would be increased in the ratio $(n/3)^{2/3}$. One way in which additional degrees of freedom of the molecules might become important could occur with molecules like the triglycerides with long chains, where three flexible chains are united rigidly at one end but are free at the other. Each of these chains might produce a thermal bombardment pressure F , like that due to single molecules of long chain compounds.

The number of factors which may affect the value of the Eötvös constant k is so great, that it is not surprising that experience has shown it to be useless as a means of determining the degree of association in a liquid.

*Variation of the Temperature Coefficient of Surface Tension
in Homologous Series.*

In 1924, guided by the kinetic considerations just outlined, and finding the data then available in the literature on the surface tension of long chain aliphatic compounds too meagre for a thorough examination of the effect of lengthening the chains, I determined the surface tension of several compounds by Sugden's maximum bubble pressure method, using the formula in his paper of 1924 *. The bubbler was immersed in a large beaker of mercury heated on gauze by a flame, and the temperature of the bath was recorded by a mercury thermometer reading to 250° , which was compared with a standard thermometer calibrated at the National Physical Laboratory, corrections being made for the exposed column. The temperatures were probably correct within one degree; no attempt was made to obtain high accuracy of temperature reading as it was desired to obtain a large number of readings as quickly as possible. Sugden's method is admirably adapted for this, as a determination of surface tension can be made well within a quarter of an hour, and the results are reproducible within 0·5 per cent. or less after very little practice, provided the apparatus is set strictly vertical. The density was determined by weighing a lump of glass suspended from a balance by a platinum hook and thread, in air and in the liquid at different temperatures ; this gave ample accuracy for the purpose, as the density only enters as a small correction. The compounds were purified or prepared here, and I have to thank Mr. J. W. W. Dyer for preparing several of them. In working with palmityl chloride, which is decomposed by

* J. Chem. Soc. p. 29 (1924).

moisture, the air current necessary for forming the bubbles was dried by drawing over sulphuric acid.

Within the temperature range investigated, the variation of surface tension with temperature was linear within the accuracy of the data, for all the substances. The results follow :—

Surface Tension of Long Chain Compounds.

Substance.	Formula.	γ at 100° C. dynes per cm.	$-\frac{d\gamma}{dT}$	Temperature range.
Caprylic acid	C ₈ H ₁₆ O ₂	{ 22·5 (21·6)	.080 (.082)	20-140
Lauric acid.....	C ₁₂ H ₂₄ O ₂	{ 24·6 (24·2)	.075 (.079)	50-150
Palmitic acid	C ₁₆ H ₃₂ O ₂	{ 25·9 (25·9)	.075 (.075)	65-170
Eicosoic acid	C ₂₀ H ₄₀ O ₂	26·7	.068	80-200
Hexadecyl alcohol.....	C ₁₆ H ₃₄ O	25·1	.078	50-180
Palmityl chloride	C ₁₆ H ₃₁ OCl	25·0	.090	20-130
α Bromopalmitic acid ...	C ₁₆ H ₃₃ BrO ₂	27·4	.072	60-150
Penterythritol tetra- palmitate } α		26·6	.064	80-190
Tetradecane	C ₁₄ H ₃₀	20·2	.085	20-150
Tricontane	C ₃₀ H ₆₂	25·4	.070	75-175

α . C(CH₂OOC.C₁₅H₃₁)₄. The Eötvös constant for this substance is 6·1.

The figures underneath mine for the first three acids, in brackets, are obtained by plotting Hunten and Maass' results. These were obtained by the method of capillary rise, and inspection of the plot shows that they lie rather less consistently on a smooth curve than mine; the discrepancy between my results and theirs is not serious except in the case of caprylic acid.

Conclusions from the behaviour of Long Chain Compounds.

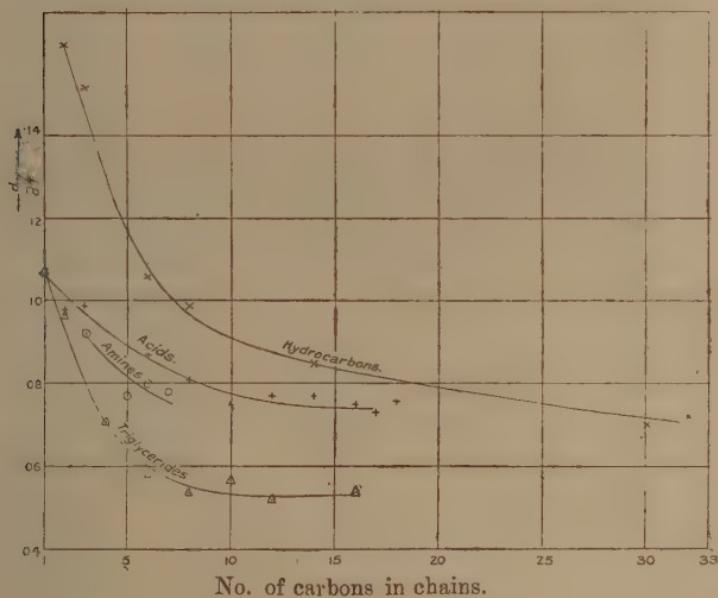
The figure shows how the temperature coefficient of surface tension, $-\frac{d\gamma}{dT}$, varies with the length of the hydrocarbon chains in the case of the four homologous series, hydrocarbons, fatty acids, normal amines, and triglycerides. The data used are, in addition to the above determinations, those of Maass and Wright* and

* J. Amer. Chem. Soc. p. 1098 (1921).

Hunten and Maass on the acids and hydrocarbons; and of Jaeger on the triglycerides and the normal amines, as well as a few data from the 'International Critical Tables,' iv.

The data gave practically constant values for $-\frac{d\gamma}{dT}$ over the

whole experimental range of temperature, except for triacetin and tributyrin, for which the points plotted are the constant values between 65° and 200° ; below 50° distinctly lower values were obtained.



All the four series have high values of $-\frac{d\gamma}{dT}$ for the shorter chain compounds, which fall asymptotically to a nearly constant value as the chains are lengthened. The limiting value for the hydrocarbons, acids, and probably the amines also, is about 0.07; the triglycerides tend to a value about 0.053, decidedly lower. The acids, triglycerides, and probably the amines approach the limiting value within experimental error when the chains are about ten carbons long; the hydrocarbons not till at least double this length of chain.

The results are most easily explained by an orientation of the molecules, which becomes nearly complete, and identical in the different series considered, when the chains are about

ten carbon atoms long, and the molecules have a polar group at one end. With the hydrocarbons, which are not loaded at one end, the orientation does not become complete until the chains are probably at least double this length. The orientation may be perpendicular to the surface, but the data indicate no more than that it is similar for all the series of single chain compounds. $-\frac{d\gamma}{dT}$, or $\frac{dF}{dT}$, measures the change in the intensity of the horizontal bombardment pressure of the surface molecules on the ideal barrier of the preceding theory. This may be expected to be exerted mainly by the long chains singly, if they are long enough; the fact that the triglycerides tend to a rather lower limiting value of $\frac{dF}{dT}$ than the single chain compounds indicates that their thermal motions *per chain* (not per molecule) are somewhat more restricted than those of the single chain compounds. This may be due either to the polar ends of the molecules contributing less per chain to F than when these ends are separated, or to some restriction on the motions of the chains, due to their being united at their bases. But as the limiting value of $\frac{dF}{dT}$ is only about 25 per cent. less for the triglycerides than for the single chain compounds, it seems that there must be a considerable amount of separate transverse motion in the long chains of the triglycerides.

Certain knowledge along these lines must await a more accurate knowledge of the kinetic theory of liquids; but these considerations are advanced as showing that we may learn more from studying the simple quantity $-\frac{d\gamma}{dT}$, in the light of the chemical constitution of the molecules, than by forming the Eötvös constant.

Summary.

The rate of decrease of surface tension with temperature, $-\frac{d\gamma}{dT}$, may be quantitatively regarded as the rate of increase, $\frac{dF}{dT}$, of the thermal bombardment pressure F, exerted by the surface molecules, parallel to the surface on a barrier in the surface. This point of view shows the

physical similarity between the rise in pressure of a gas and the fall in surface tension of a liquid, as the temperature rises.

The development of this theory shows that the following factors, besides molecular association, will probably affect the value of the "Eötvös constant"

$$\frac{d}{dT} \left\{ \gamma(Mv)^{2/3} \right\} :$$

orientation of the surface molecules, the number of molecules in the thickness of the surface layer, the number of their degrees of freedom as regards motions which can produce thermal bombardment, and all properties which may cause the thermal bombardment pressure in the surface to differ from that of a perfect two-dimensional gas, which will include chemical attractions between the surface molecules and details of their shape and size. As these factors, particularly the last two, cannot be evaluated at present, it is not surprising that Eötvös' rule has been shown in practice to be quite untrustworthy for determining the molecular association of liquids.

The temperature coefficient of surface tension of four homologous series is considered, and some new data presented for long chain compounds. There appears to be nearly complete orientation of the surface molecules when the chains are ten carbons or more long, if the molecules have a polar group at one end; the hydrocarbons are probably not fully oriented till double this length of chain. The intensity of vibration of the molecules of the triglycerides appears to be somewhat less than that of three chains separately, although the chains clearly move independently to a large extent.

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LVII. *The Heats of Dissociation of some Strong Electrolytes in Benzonitrile and their Calculation from Molecular Structure.* By A. R. MARTIN, Ph.D.*

M EASUREMENTS of the dielectric constant of benzonitrile over the temperature range 0° to 70° C., for which the author is indebted to Dr. A. O. Ball, make it possible to calculate the dissociation constants of strong electrolytes in this solvent from conductivity data by the method and from the data published previously †, and from

* Communicated by Prof. J. C. Philip, F.R.S.

† Martin, J. Chem. Soc. p. 3270 (1928).

the variation of the dissociation constant with temperature to calculate the heats of dissociation by means of the van't Hoff Isochore.

The values of the dielectric constant of benzonitrile (D), determined by a bridge method at a frequency of 1000 cycles per second, are as follows:—

Temp.....	0°	25°	40°	50°	55°	70° C.
D.	27.58	25.22	24.04	23.31	22.96	21.98.

In Table I. are given the dissociation constants, corrected for activity, of the following electrolytes in benzonitrile

TABLE I.

Electrolyte and Temperature.	Dissociation Constant $\times 1,000$.					
	Dilution (litres).					
	5000.	2000.	1000.	500.	100.	Mean.
LiI.	• C.					
	0.....	5	5	5	5	5
	25.....	10	9	7	7	8
	50.....		10	8	7	9
NaI.	0.....		8	10	12	10
	25.....		15	15	13	14
	50.....		13	10	10	11
	70.....		15	10	7	10
KI	0.....		18	14		16
	25.....	13	10	10		11
	40.....	7.2	7.3	7.2		7.2
	55.....	6.7	6.6	6.6		6.6
	70.....	6.1	6.1	5.9		6.0
LiBr.	0.....	0.35	0.30	0.26	0.26	0.29
	25.....	0.36	0.34	0.27	0.29	0.31
	50.....	0.35	0.31	0.25	0.26	0.29
	70.....	0.32	0.25	0.23	0.23	0.26
AgNO ₃	0.....	0.39	0.46	0.48	0.53	0.48
	25.....	0.40	0.40	0.40	0.39	0.42
	40.....	0.34	0.34	0.34	0.34	0.39
	55.....	0.32	0.33	0.33	0.32	0.33

over the temperature range 0° to 70° C., the iodides of lithium, sodium, and potassium, lithium bromide, and silver nitrate.

The foregoing mean values of the dissociation constants yield the values of the heats of dissociation given below. The values of the dissociation constants at 0° C. are not as trustworthy as at the other temperatures, since the differences between the observed and theoretical values of the equivalent conductivity are smaller at this temperature than at

the others. For silver nitrate the heat of dissociation may be quoted to 0·1 k. cal., but for the other more strongly dissociated salts, where the values of the dissociation constants are less certain, the heats of dissociation may be quoted only to the nearest k. cal.

Electrolyte	LiI	NaI	KI	LiBr.	AgNO ₃
Heat of dissociation in k. cals. } +2 -1 -3 0 -1·4					

The heat of dissociation of an electrolyte in any solvent may be calculated from theoretical considerations in the following way. The dissociation may be imagined to be carried out in three stages, (1) removal of the undissociated molecule, which is an electrical dipole, from the solvent to a vacuum or air, (2) dissociation of the vapour molecule in a vacuum or air, and (3) solvation of the resulting ions.

The energy change in process (2) for certain atomic ions has been calculated by Born and Heisenberg *. Born and Heisenberg take into account the inverse square attraction, the inverse 9th power repulsion, and the attraction due to the dipoles set up by the mutual deformation of the ions. They show that the heats of formation of undissociated vapour molecules so calculated agree well (1 to 5 per cent.) with the difference between the lattice energy and the experimentally determined heat of sublimation of the salt. The effects of ionic deformation are responsible for 10 to 20 per cent. of the energy of formation of an undissociated vapour molecule.

The energy change in process (3) has been calculated by Born †, by considering the change in the energy in the medium resulting from the transfer of the ion, treated as a charged sphere, from a vacuum or air, that is from a medium of dielectric constant unity, to a medium of dielectric constant D. This energy change, in k. cals. per mol, is given by

$$\frac{z^2 e^2}{2r} \left(1 - \frac{1}{D}\right) \frac{N}{J} \quad \dots \quad (1)$$

where, e =the elementary charge of electricity;

N =the Avogadro number;

J =the mechanical equivalent of heat (ergs per k. cal.);

z =the valency of the ion;

r =the radius of the ion.

* Born and Heisenberg, *Z. f. Physik*, xxiii. p. 388 (1924).

† Born, *Z. f. Physik*, i. p. 45 (1920).

Born has shown that from the heats of hydration of ions obtained by the method of Fajans* values of r of the correct order of magnitude can be calculated by means of equation (1).

The energy change in process (1) may be calculated as follows. Consider a small electrical dipole in a medium of dielectric constant D . If the dipole is sufficiently small the electric field, E , at any point P is given by

$$E = \frac{M}{Dr^3} \sqrt{1 + 3 \cos^2 \theta}$$

where, M = the moment of the dipole;

r = the distance from P to the mid point of the dipole;

θ = the angle between r and the axis of the dipole.

The energy per c.c. of the medium is

$$\frac{DE^2}{8\pi} = \frac{M^2(1 + 3 \cos^2 \theta)}{8\pi Dr^6}.$$

The element of volume swept out by the element of area dS , in polar coordinates, at P in rotating about the axis of the dipole is

$$2\pi r^2 \sin \theta dr d\theta,$$

and since from symmetry every portion of this annulus is similarly situated with respect to the origin, the electric field at every point in it is the same, and the energy contained in the annulus is

$$\frac{M^2(1 + 3 \cos^2 \theta)}{4Dr^4} \sin \theta dr d\theta.$$

Therefore the total energy in the medium around the dipole is

$$\sum_{\substack{\theta=\pi \\ r=\infty}}_{\substack{\theta=0 \\ r=a}} \frac{M^2}{4Dr^4} (1 + 3 \cos^2 \theta) \sin \theta dr d\theta.$$

where a is some function of the size of the dipolar molecule,

$$= \frac{M^2}{4D} \int_{r=a}^{r=\infty} \int_{\theta=0}^{\theta=\pi} \frac{1}{r^4} (\sin \theta + 3 \cos^2 \theta \sin \theta) dr d\theta.$$

* Fajans, *Verh. Deut. phys. Ges.* xxi. pp. 549, 709 (1919).

The evaluation of this integral is

$$\frac{M^2}{3Da^3}.$$

Therefore the energy change in removing the dipole from a medium of dielectric constant D to a vacuum or air is, in k. cals. per mol,

$$-\frac{M^2}{3a^3}\left(1 - \frac{1}{D}\right)\frac{N}{J} \dots \dots \dots \quad (2)$$

The lower limit of integration a , the distance from the origin at which the medium commences, has been taken equal to the radius of the sphere of volume equal to the volume of the dipolar molecule.

Owing to the uncertainty of the numerical values to be assigned both to a , which enters into the calculation cubed, and to the radii of the free ions, the following procedure has been adopted in applying these theoretical results to the present data. The values of M and of the heats of dissociation in a vacuum have been taken from Born and Heisenberg's paper. The volume of the undissociated molecule has been calculated by taking the distance apart of the nuclei of the ions given by Born and Heisenberg to be the sum of the ionic radii, and by assuming that the radii of the cation and anion bear the same ratio to each other in the dipole as in the crystal lattice. The heat of removing the undissociated molecule from the solvent and of dissociating it in a vacuum having thus been calculated, the value of the heat of solvation of the ions required in order that the calculated may equal the observed value of the heat of dissociation in the solvent was found. The free anion was assigned the radius given by Goldschmidt*, and its heat of solvation calculated. By subtracting this from the total heat of solvation required, the required heat of solvation, and hence, from equation (1) the radius, of the free cation was calculated. The dielectric constant of benzonitrile has been taken as 25.

In Table II. are given the results of these calculations for sodium and potassium iodides, together with the values of the ionic radii obtained from crystal data by Goldschmidt* (which are in close agreement with those calculated by Pauling† from the wave mechanics). It is impossible to perform the calculations for the other salts, since Born

* Goldschmidt, Trans. Faraday Soc. xxv. p. 253 (1929).

† Pauling, J. Amer. Chem. Soc. xlix. p. 765 (1927).

and Heisenberg's calculation cannot at present be carried out for polyatomic or for lithium ions.

TABLE II.

	Sodium Iodide.	Potassium Iodide.
Distance between the nuclei in the undissociated molecule (cms.)...	2.59×10^{-8}	2.86×10^{-8}
Radius of the anion in the undissociated molecule (cms.)	1.79×10^{-8}	1.79×10^{-8}
Radius of the cation in the undissociated molecule (cms.)	0.80×10^{-8}	1.07×10^{-8}
Radius of the sphere equal in volume to undissociated molecule (cms.)	1.84×10^{-8}	1.92×10^{-8}
Dipole moment of the undissociated molecule (e.s.u. and cms.) .	1.24×10^{-17}	1.36×10^{-17}
Heat of removing the undissociated molecule from benzonitrile to a vacuum k. cals. per mol)	-114	-123
Heat of dissociation in a vacuum (k. cals. per mol)	-126	-113
Heat of solvation of the ions required (k. cals. per mol)	+239	+233
Radius assigned to the free anion (cms.)	2.20×10^{-8}	2.20×10^{-8}
Heat of solvation of the free anion (k. cals. per mol)	+72	+72
Heat of solvation of the free cation required (k. cals. per mol).	+167	+161
Radius of the free cation required (cms.)	0.95×10^{-8}	0.99×10^{-8}
Radius of the cation (Goldschmidt) (cms.)	0.98×10^{-8}	1.33×10^{-8}
Radius of the anion (Goldschmidt) (cms.)	2.20×10^{-8}	2.20×10^{-8}

The agreement between the observed and calculated values of the ionic radii is satisfactory, considering the approximations which have been made in the calculations. It therefore appears probable that an undissociated molecule of a strong electrolyte in a solvent is the same as the undissociated vapour molecule, that is a pair of deformed ions in contact with each other, there being no intervening medium.

LVIII. Ionization Currents from Zinc Oxide Smokes.
*By H. P. WALMSLEY, M.Sc.**

THIS paper describes the ionization currents from clouds or smokes of zinc oxide particles and is supplementary to earlier work on the currents from clouds of cadmium oxide particles. A zinc oxide smoke is produced in a large cistern from say, an electric arc between zinc electrodes. The ionization initially and its time changes as the smoke ages are measured.

The general arrangement of the apparatus used and the manner of working have been described previously¹. A steady flow of smoke from the cistern was passed through an ionization vessel consisting of two concentric cylinders. The outer cylinder was connected to one terminal of a battery giving up to 1,000 volts, to produce an electrostatic field within the vessel. The inner cylinder was connected to a Dolezalek electrometer. The currents were measured either by the time rates of the deflexions, or by shunting the inner cylinder to earth through a high resistance and measuring the differences in potential between the two ends of the resistance. The rate of flow of smoke through the ionization vessel was measured directly by the rate of efflux of water from the constant head aspirator producing the flow. It was found that flow-meters, particularly of the Venturi type, were unreliable, as constrictions in the circuit tend to get clogged with deposited particles.

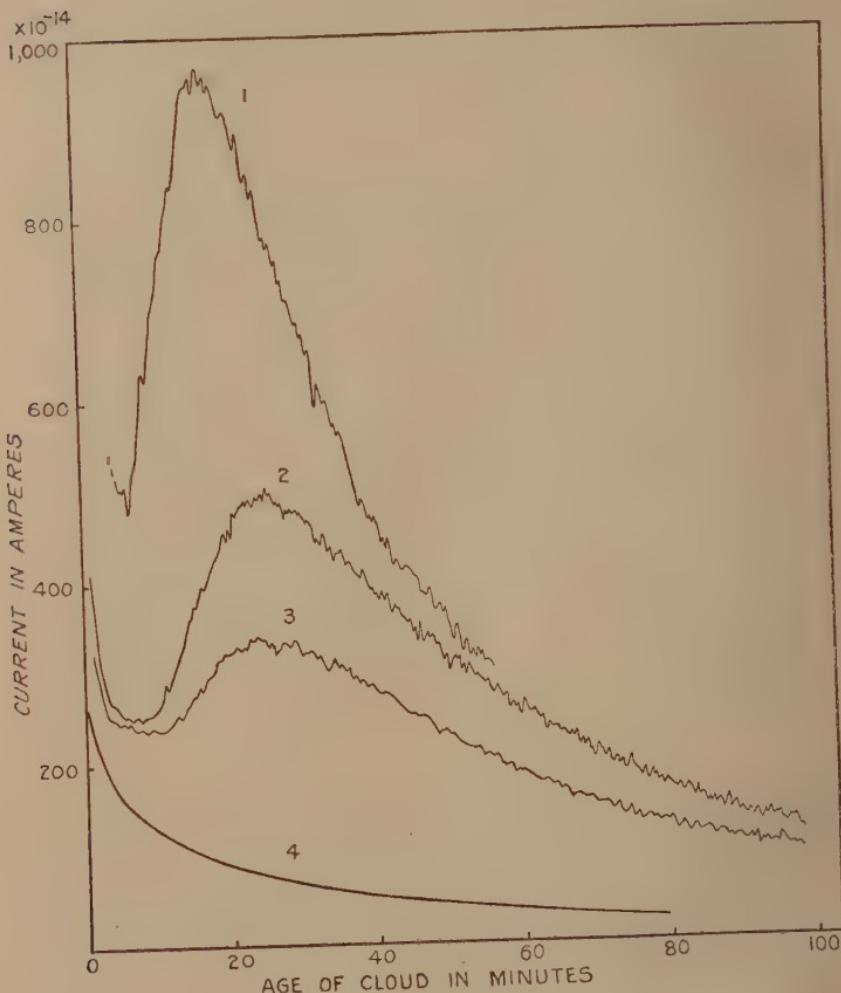
Smokes dispersed from a Zinc Arc.

A series of smokes of increasing weight concentration produced from an arc between zinc electrodes was examined. The increases in the mass of material dispersed were obtained by keeping the conditions at the arc as nearly as possible constant throughout the series and allowing the current to flow for increasingly longer periods of time ranging from 10 seconds to 40 seconds. The absolute values of the concentrations are unknown. There is no simple and satisfactory method of measuring this quantity. To ensure homogeneity of the cloud, the fan in the cistern

* Communicated by the Author.

was kept running for some time after the smoke had been dispersed. Measurements of the ionization current were made from immediately after dispersal was complete until the currents became negligibly small. The rate of flow of

Fig. 1.



smoke through the ionization vessel was constant and the same in each run and the electric field was sufficient to give the saturation value of the current for all ions entering it of mobility greater than $1 \times 10^{-4} \text{ cm}^2./\text{sec. volt.}$

The curves of fig. 1 show how, after dispersal, the ionization currents from negative carriers for four smokes of the series change with time. The currents were measured by the steady deflexion method and are represented by the ordinates, the unit being 10^{-14} ampere. Their numerical values are roughly equal to the deflexions observed in scale-divisions (mm.). Curve 1 was obtained from the smoke of greatest concentration. This filled the smoke chamber with a dense fog. Curve 4 was obtained from the smoke of least concentration. This was invisible in the smoke chamber. Curves 1, 2, 3 are oscillatory and show that at some time after the dispersal process has been completed, the current strength increases to a maximum before it ultimately diminishes. The fluctuations in curve 4, however, are only of the order of magnitude of the fortuitous movements of the electrometer needle about the zero, due to unsteadiness. In other words, the curve is indistinguishable experimentally from one which would be given by a smooth continuous process. The currents obtained from zinc oxide particles are therefore like the ones obtained from cadmium oxide particles produced under similar experimental conditions⁽²⁾.

The behaviour of the ionization currents is closely associated with the behaviour of the particles which form the smokes. The primary particles of a smoke dispersed from a metallic arc diminish in number by a process of aggregation, whereby complex particles (aggregates) are produced. There is also a loss due to sedimentation of the heavier particles. Further, it is known both by direct observation with the ultramicroscope and from estimates of the mobilities of the ions, that the electrical charges are carried at least partially by the particles. Provided the particles are small enough, the charges carried can influence the rate of aggregation, but in most smokes a stage must ultimately be attained when their influence is negligible. There are reasons for supposing that the initial electrification of the primary particles is a secondary effect as regards the behaviour of the disperse system. The charges themselves are supposed to originate from thermal emissions at the high temperature of the arc and to combine afterwards with the primary particles formed simultaneously. This would account for the fact that the particles are not all charged and is supported by the observations of Erikson⁽³⁾ and others on ions emitted

from hot metals. For example, it is found that although the initial positive ion emitted from hot platinum during an interval of the order of one-third of a second from birth usually changes over into a normal ion of mobility 1.36 cm.² sec. volt. identical with the normal ion produced in air by the α rays from polonium, if the temperature of the platinum is very high and the ions are allowed to remain for a short time in the air which has left the platinum surface, they load up and form heavier ions. That is they unite with the particles which are known to be produced from a platinum surface under these conditions. The electrons and initial positive charges emitted by the arc during the dispersal process have the option of uniting with gas molecules to form normal ions and of uniting with primary particles. Their distribution as normal ions and charged particles depends upon the relative collision frequencies, the greater probability of a collision with a particle in the latter case being discounted on most occasions by the relatively much greater number of gas molecules. Thus we may consider that a smoke consists initially of a collection of charged and uncharged primary particles and of normal ions, which may disappear by uniting with particles subsequently and by recombination amongst themselves.

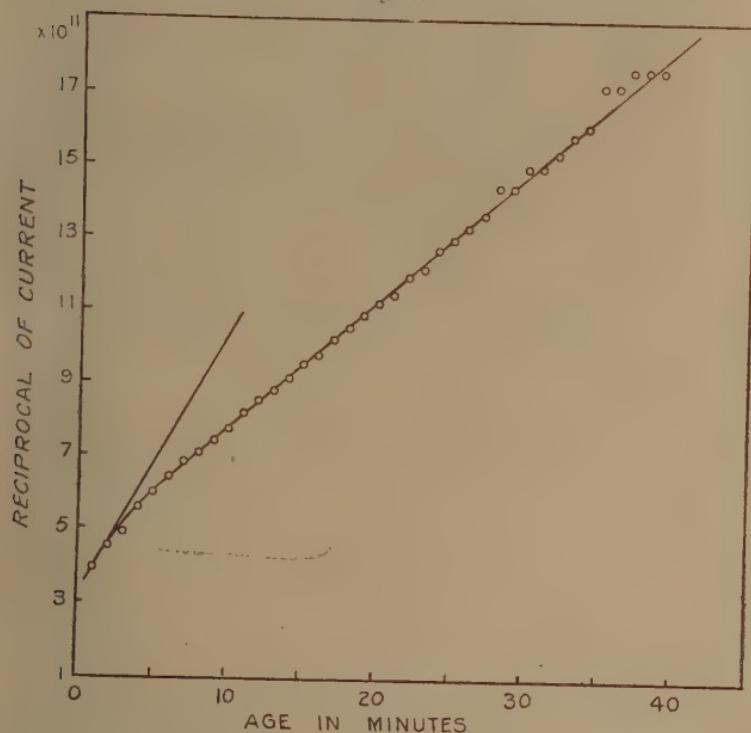
As the cloud ages, the process of aggregation of the particles, together with the loss of normal ions by combination with particles, produces carriers of varying and diminishing mobilities in the smoke. The loss of mobility of the charges of itself causes little diminution with time in the measured current strength, if the field in the ionization vessel is sufficiently intense to give continuously the saturation current from the stream passing through it; but a decrease begins of course, as soon as groups of charged particles are formed whose mobilities are so low that the velocity impressed upon a group by the field is insufficient to drive the whole of the carriers into the collecting electrode. Sedimentation and diffusion to the walls in the main body of the smoke also affect the currents measured, but the principal loss arises from the recombination of unlike charges on the normal ions and the particles. These effects account for the initial falls in current strength in the curves of fig. 1. Some of them are illustrated in more detail in what follows.

Recombination of the Initial Charges.

Fig. 2 shows how the reciprocal of the current varies with time for the smoke of curve 4, fig. 1. For a short period the curve is concave to the axis of time, but afterwards it is practically linear. The number N of negative charges per unit volume of the smoke at time t can therefore be represented by the equation

$$\frac{1}{N} - \frac{1}{N_0} = \beta t$$

Fig. 2.



where N_0 is the initial number of negative charges. The value of β diminishes where the curve is concave, but it is constant over the linear portion. The most probable cause of the early curvature is that α , the coefficient of recombination of the charges, is diminishing in a similar way to the quantity β . This means that the mobilities of the carriers are diminishing as the smoke ages and/or that the ratio of the number of collisions which result in

recombination to the total number occurring between carriers of unlike charges decreases with time⁽¹⁾. The quantity α is no longer a specific constant appropriate to a given type of ion, but is an average value which is changing with time. If the initial number of positive and negative carriers were unequal and α were constant, the curve of fig. 2 would be convex to the axis of time. It is probable from their origin that actually there is an initial excess of one kind of electricity, but it is not known with certainty whether an excess was present in this particular case. If there is a production of charges in the smoke after dispersal has ceased, and it will be seen later that this is the case, it is evident that a system which would otherwise obey the ordinary law of recombination and give a straight line when the reciprocal of the current is plotted against time, will now give a curve concave to the axis of time. The effects of sedimentation and diffusion, like inequality of the initial charges, tend to make the curve convex to the axis of time. As the observed curve is the resultant effect, it is obvious that β is a very complex physical quantity, although from fig. 2 it appears simple empirically. With denser smokes of course, e.g., that of curve 3 (fig. 1), the curvature becomes increasingly noticeable. The numerical value of β in fig. 2 varies from $7 \cdot 0 \times 10^{-10}$ (the tangent) to $3 \cdot 6 \times 10^{-10}$ for the linear portion of the graph, where the second has been taken as the unit of time and the elementary charge as $4 \cdot 77 \times 10^{-10}$ E.S.U. The quantity β is therefore of much smaller magnitude than the coefficient of recombination for ions produced in air by X-rays. The value of the latter is $1 \cdot 6 \times 10^{-6}$. Therefore, if we assume that with clouds of very low concentration the order of magnitude of β is equal to that of α , the coefficient of recombination of the ions in the cloud, the mean mobility must be of the order of 10^{-4} cm.²/sec. volt, since the coefficient of recombination is approximately proportional to the sum of the mobilities of the positive and negative carriers. Obviously the carriers of the charges in a smoke are large.

The close connexion between the particles and the charges makes a comparison of the rate of decay of the current with the rate of coagulation of a smoke of interest. The latter has been measured for smokes dispersed from various substances of low vapour-pressure by Green⁽⁴⁾ who used a method based upon the Aitken effect, and by

Professor Whytlaw-Gray⁽⁵⁾ and his collaborators, who used a modification of the Zsigmondy slit ultramicroscope to count the particles. It is found that the number n of particles per unit volume diminishes with the age t of a smoke according to the formula

$$\frac{1}{n} - \frac{1}{n_0} = Kt,$$

where n_0 is the initial number of particles per unit volume and K is a constant for a given cloud. As with β , it is found that K varies slightly from cloud to cloud. The mean of the values quoted by Green for ammonium chloride smokes is 9.5×10^{-10} and for cadmium oxide smokes it is 7.7×10^{-10} , using the second as the unit of time. Whytlaw-Gray's values for a series of smokes from each of four substances, NH_4Cl , As_2O_3 , antipyrin, and CdO range from 5.0×10^{-10} to 10.0×10^{-10} with a mean about 7.3×10^{-10} . These quantities are of the same order of magnitude as the values for β in the smoke of fig. 2. It therefore seems that with clouds of low mass concentration, the rate of decay of the current is controlled mainly by the rate of aggregation of the particles. To a first approximation, the chance of a negatively charged particle uniting with a positively charged particle and thereby entailing the loss of a negative charge is equal to the chance of two uncharged particles colliding and uniting, causing the loss of a particle.

On theoretical grounds it is to be expected that, in the very early periods of the life of a smoke, the initial charges will disappear at a greater rate than the smoke particles, but that later, as they become attached to particles, the rate will approximate to that at which the particles disappear. This results from the size of the particles. An accurate comparison of the values of β and K would be of value but it requires two sets of observations upon the same cloud.

The concomitant disappearance of charges and particles according to the preceding formulæ has been observed by Kennedy⁽⁶⁾ in the case of the large ions and condensation nuclei from a bunsen flame, where the particles are probably liquid. Kennedy's values for the quantities β and K were 6.3×10^{-10} and 14.0×10^{-10} respectively. Here the mobility of the large ions was found to be .0003

cm.² sec. volt, and the mobilities of all the ions were the same.

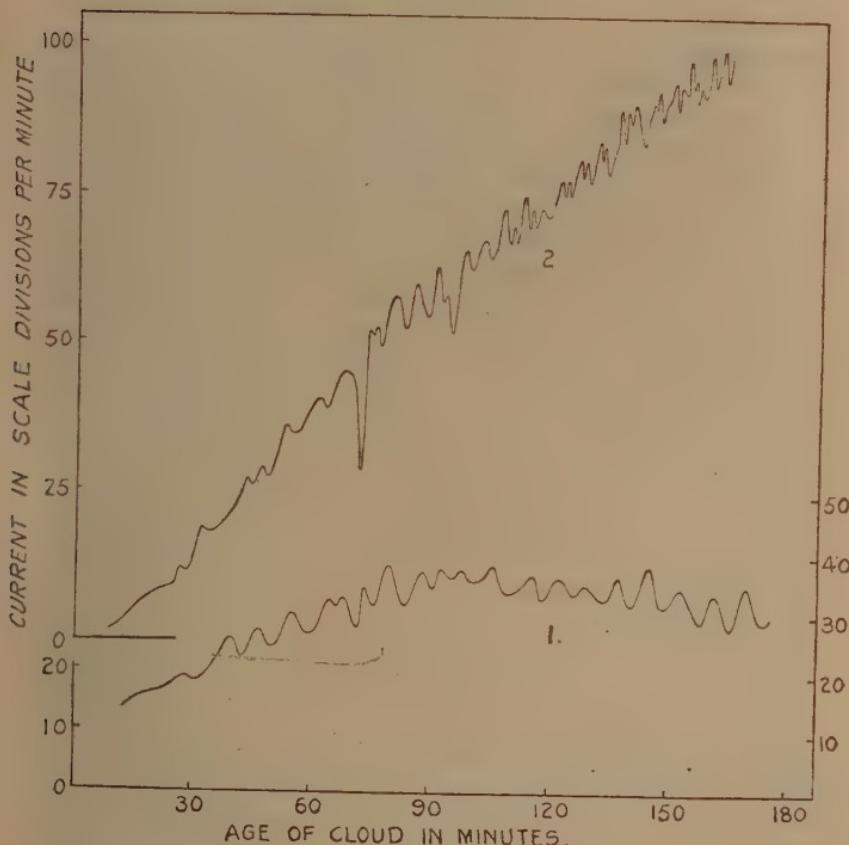
Ionization produced in the Smokes after dispersal.

When the mass of material dispersed is increased, fig. 1 shows that the ionization curves change their form. After the initial fall, the current rises again and passes through a maximum before settling down into a general decrease with time. It can be shown by the same methods which were used in the case of cadmium oxide smokes, that the rise in current strength is due to a production of ions in the smoke as it ages. To explain the curves the following theory was proposed⁽²⁾. It is supposed that the complex particles produced by the process of aggregation are not all stable and that the unstable complexes are liable to break up again, presumably under the influence of molecular bombardment by the gas molecules of the medium. When this occurs new charges appear. The intensity of the ionization so produced and the total number of complex particles in the smoke are assumed to change with time in a similar way. The intensity is therefore zero initially. It rises to a maximum and afterwards diminishes as the cloud ages. The total ionization at any moment in the life of a cloud thus consists of two parts, the charges remaining from the initial ionization which accompanied the formation of the primary particles and the charges produced by the disruption of unstable aggregates which have formed during the process of coagulation.

It has been shown with the smokes from many metals⁽⁷⁾, and it is probably true for all, that the formation of the primary particles dispersed from an arc takes place at a high temperature. It has also been assumed that the initial charges are adventitious and arise from thermo-electric emissions at the high temperature of formation. The initial ionization ought to be eliminated therefore if we could disperse the same kind of particles at comparatively low temperatures, when we should obtain a system containing no ions initially, in which a spontaneous production of ions occurs as it ages. Such a system is obtained if the zinc oxide is dispersed by the decomposition of diluted zinc ethyl vapour in air. Fig. 3 shows two typical ionization curves for zinc oxide clouds produced in this way.

The zinc ethyl vapour was passed into the cloud chamber with a current of nitrogen. This was used so that the composition of the medium would be altered as little as possible from that of dry dust-free air. Nitrogen from a cylinder of the compressed gas, freed from oxygen and moisture in the usual way, passed through a flow

Fig. 3.



meter and dust filter along a tube which opened centrally in the cistern. A branch circuit was arranged between the flow meter and filter so that the gas stream could be deflected through a large bottle containing a little liquid zinc ethyl. The procedure adopted to disperse a series of clouds of increasing concentration was the following. Nitrogen was passed into the chamber at a fixed rate for a given period of, say, 10 minutes each run. During this period

the gas stream was diverted through the bottle containing the zinc ethyl for increasingly longer times up to 8 minutes. The nitrogen which passed into the chamber before the stream was deflected along the branch circuit swept the discharge tube free from air, and that which passed after the flow was redirected along the main circuit cleared the discharge tube from traces of zinc ethyl vapour. Equal quantities of nitrogen were used for the two operations in any given case so that the middle of the period of 10 minutes could be made the arbitrary zero of time for computing the age of the cloud. After dispersal, the currents were measured under precisely the same conditions as those in fig. 1. The currents obtained from all the smokes examined were very much weaker than those obtained from smokes dispersed from an arc, so they were measured by time rates of deflexion. To increase the number of observations on a given smoke, several measurements were made in succession each time the electrometer needle was set in motion. The measurements therefore occur in groups which can be fairly readily picked out on the graphs. These are drawn to include every observation.

Curve 1 (fig. 3) shows the results obtained from a smoke in which the zinc ethyl was at 15.5°C . during the dispersal process. The general trend of the current is from zero initially to a maximum at about 90 minutes, after which a slow diminution in current occurs. The curve is therefore of the form anticipated.

It was found that with the zinc ethyl at room temperatures, increasing the concentration of the smoke by the method already described did not cause any great changes in the currents measured. The ordinates of the curves which represented the smoothed out mean current at any age increased towards a maximum as the concentration increased but afterwards tended to diminish. The diminution occurred first where the age of the cloud was great and progressed gradually towards the origin of time, thus causing the current curves for larger concentrations to fall off more rapidly and intersect the curves from the weaker smokes. One would expect this effect if the masses of the particles rather than their number increased with increasing concentration and if the field strength employed was insufficient to ensure saturation. The same effect was observed in a series in which the nitrogen was replaced

by carbon dioxide, the general characteristics being similar. It is highly probable that this results from the relatively long time occupied in dispersing the cloud. The particles formed by the decomposition of the first portions of the zinc ethyl vapour as it comes in contact with the air in the chamber are distributed by the fan which is kept running to ensure homogeneity of the smoke. Hence, the later portions of the vapour decompose in a medium containing zinc oxide particles, which will undoubtedly act as centres of condensation and preferentially collect the molecules of zinc oxide which result from the reaction. This tends to increase the average mass of the particles rather than their number as the duration of the reaction is increased. It may be pointed out that cadmium oxide particles act in this way as nuclei for the condensation of cadmium oxide vapour¹⁸. The effect seems to have been observed more directly by Green¹⁴. He finds that the initial number of particles in an ammonium chloride smoke dispersed by volatilization in dust-free air increases very slowly with the concentration; *e.g.*, a tenfold increase in the latter gave an increase of about one third in the number of particles per unit volume. He explains this result on similar lines.

It was found that increasing the vapour pressure of the zinc ethyl leaving the discharge tube increased the ionization of the cloud. The bottle containing the zinc ethyl in the branch circuit was immersed in a bath of warm water and to prevent loss of vapour as it was carried through the filter by the nitrogen, the filter and the exposed parts of the discharge tube were raised to a higher temperature. Curve 2 of fig. 3 shows the currents obtained when the temperature of the bath was 35° C. and the time of flow of vapour was 2 mins., all other conditions being precisely the same as for curve 1, where the temperature was 15.5° C. and the time of flow 9 mins. The current rises as before and approaches a maximum nearly three times as great as the previous value, at about three hours after dispersal. Had measurements been continued longer the current would have been found to decrease.

If we assume von Weimarn's law of corresponding states to hold for the reaction with zinc ethyl in dust-free air, the increased vapour pressure in the case of the cloud of curve 2 will give a higher degree of dispersion than the reaction for the cloud of curve 1, that is, the particles

will be finer. The shorter time involved in dispersal will tend to enhance the difference in size since the particles first formed in the reaction are less likely to act as condensation nuclei for those formed later. The total mass of oxide produced will probably not differ much in the two cases, so there is a corresponding increase in the number of particles per unit volume in the cloud of curve 2. It is probable therefore that in this cloud the particles are both more numerous and smaller than in the cloud of curve 1 and it is tempting to ascribe to this the difference in intensity of the ionization.

The general shape of the two curves is the same and if we attribute the difference in quality to the degree of dispersion—the average size and distribution of sizes amongst the particles—we seem able to account for the failure at present to produce from zinc ethyl, clouds giving currents of the intensity of those attributed to the disruption of complexes in the clouds produced from a zinc arc. The supersaturation in the arc must be vastly higher than anything yet attained with zinc ethyl. The point established by the experiments is that there is a formation of ions in zinc oxide clouds as they age and that this is quite independent of whether the clouds are ionized on formation or not.

The Nature of the Zinc Oxide Particles.

The question whether the same kind of particles was produced by the decomposition of zinc ethyl and by the electric arc was decided by X-ray analysis. The dispersed particles were precipitated electrically by an intense field and a sample from each source was examined by the powder method using $\text{CuK}\alpha$ radiation. Each gave a spectrum characteristic of a crystalline powder, although the lines were rather diffuse on account of the small dimensions of the individual particles. Their positions and intensities were in close agreement with those recorded by Weber⁽⁹⁾. The closest agreement between the observed and calculated values for the spacings measured was obtained with an axial ratio of $\gamma = 1.605$ which led to a mean value of $a = 3.250 \text{ \AA}$. Thus the lattice constants are $a = 3.250 \text{ \AA}$, $c = 5.217 \text{ \AA}$, whence $\rho = 5.62 \text{ grams/cm}^3$. These agree with Weber's values, $a = 3.251 \text{ \AA}$, $c = 5.226 \text{ \AA}$, slightly better than with the more recent ones of Barth⁽¹⁰⁾, $a = 3.242 \text{ \AA}$, $c = 5.176 \text{ \AA}$. The particles produced by both

reactions are therefore identical. They are minute crystals of the normal structure and density of zinc oxide in the crystalline form—zincite, and the complex particles are crystal aggregates, most probably dendritic in form.

Incidental Observations.

In the preceding experiments the currents were obtained from a portion of cloud in motion through a metal tube. Now it is well known that wet steam, that is steam containing liquid particles, impinging on a solid surface gives rise to electrification although dry steam or dry gases do not. This suggests that the motion of the cloud in the apparatus may have some effect on the currents measured. Again when fine dusts are dispersed by an air blast the particles become charged, the electrification being usually attributed to a frictional effect between the particles and the medium. We have to decide therefore whether the currents measured arise from the motion of the cloud or not. If they do, the charges in the case of a cloud produced from zinc ethyl may be attributable to a triboelectrical effect. If not, that cloud provides us with a system which has the novel property of ionizing itself spontaneously. Although it is probable that the ionization in smokes has a very close connexion with the electrification produced in dusts by an air blast, it is clear from the dependence of current strength upon the age of a cloud that more is involved in the production of cloud ionization than the mere rubbing of the medium against the surfaces of the particles. The following additional results on the cloud of curve 2 (fig. 3) seem to support the view that the ionization process is spontaneous.

(a) At 2 hr. 44 mins. the current from the smoke was 98 units. At 2 hr. 45 mins. a two-way tap immediately in front of the ionization chamber was turned and the flow of cloud was replaced by a flow of dry dust-free air entering at exactly the same rate as the cloud. The current immediately dropped and at 2 hr. 46·6 mins. was represented by 7·7 units. A later reading could not be obtained.

(b) At 2 hr. 48 mins. the tap was turned back again and the cloud allowed to pass into the ionization vessel. The following table shows the currents registered at times later.

0	0 ^m 40 ^s	1 ^m 18 ^s	1 ^m 54 ^s	2 ^m 30 ^s	3 ^m 0 ^s	
0	57·1	77·6	86·6	87·4	89·1	divs./min.

(c) At 2 hr. 52 mins. the flow was again stopped and the currents from the sample of cloud left behind in the ionization chamber were measured. Times are subsequent to 2 hr. 52 mins.

1 ^m	0 ^s	2 ^m	14 ^s	6 ^m	12 ^s	13 ^m	7 ^s
83.4		78.3		75.0		73.2	divs./min.

On the hypothesis that the ionization was a frictional effect and provided we had a constant intensity of ionization and that all ions entering the electric field were driven to the electrodes, we should expect the currents (a) and (c) to be almost identical : for the ions present within the field at the moment the conditions are changed should be collected in the same time whether they possessed a component velocity at right angles to the field or not, and the total charge collected after the change should be the same in both cases. Further, the currents (a) and (c) should be complementary to (b). Since (a) and (c) are grossly dissimilar, we conclude that either the current is unsaturated. *i. e.*, we are collecting in (c) ions which pass completely through the field under the conditions in (a) ; or the cloud at rest in (c) produces ions as it ages.

Assume the current is unsaturated. Let E be the difference between the values of the total charge collected in (a) and (c) and let V be the volume of the ionization vessel. The ratio E/V measures the average charge per unit volume which passes completely through the field. This may be compared with the charge per unit volume actually collected from the steady flow. From the data available $\int idt$ can only be evaluated for 13 mins. in the

case of (c) but this will be sufficient for our purpose. We find $E = 990 - 40 = 950$ units (divs./min. \times mins.). The current from the steady flow was 90 divs./min. (limiting value in (b)) and the rate of flow was $3.0 \times V$ c.c./min. The charge collected from V c.c. is 30 units, which is approximately 3 per cent. of the total charge in unit volume of the smoke. But the field gives the saturation current from all ions entering it whose mobilities are greater than 1×10^{-4} cm.²/sec. volt, so the assumption leads to the result that over 97 per cent. of the charges are carried completely through the field on ions with mobilities less than 1×10^{-4} cm.²/sec. volt. This is improbable.

On the same assumption, a lower limit to the mobility of the ions is given by the time taken for the current to disappear, for this is the time required for the slowest moving ions present, when the flow is stopped, to cross the field. The time may be very great. In fig. 4 of an earlier paper¹, a case is shown where this is at least 100 minutes, corresponding to a mobility of 1.4×10^{-8} cm.² sec. volt—the mobility of a spherical particle of radius 3.4×10^{-2} cm. charged with one electron. Since the ionization vessel is horizontal and the diameter of the outer cylinder less than two cm., particles of this size could not remain suspended in the field for 100 mins. We must conclude therefore that the slow decay of the current from a sample of cloud at rest in the electric field is due to ions produced in the field as the cloud ages. It is part of the process which gives the currents measured in fig. 3.

From this it appears that in the experiments of figs. 1 and 2, the zinc oxide clouds were actually producing ions in their passage through the ionization vessel. The corollary follows that we can never obtain "saturation" currents, for only a field of infinite intensity can collect all the ions from cloud in motion through it. This is a source of difficulty in the interpretation of experimental results.

Smokes of low mass concentration dispersed from a zinc arc give similar results. When the flow of smoke is replaced by dust-free air the current rapidly disappears. When the concentration is greater and the change is made after the current from the cloud has passed through the maximum, it is found that although the current falls rapidly at first, it often persists at an appreciable magnitude for a considerable time. It has been measured for as long as one hour after the change to dust-free air has taken place. If the cloud acted like a perfect fluid in its motion through the electric field, the cloud and the current due to ions received from it should disappear in the time (20 secs.) taken for V c.c. to pass through the field. Owing to viscosity the cloud is not swept out so quickly. The fraction remaining at any time can be calculated and it is found that the current disappears at a considerably slower rate. The excess current must arise from the zinc oxide particles deposited on the walls of the ionization vessel. Since the charges in the cloud are carried mainly by particles, the field collects particles when collecting charges. These form crystal growths on the electrodes

which apparently are able to produce ions in the cloud itself. Hence the currents measured in the experiments of figs. 1 and 3 are contributed partly by the cloud passing through the ionization chamber and partly by the deposit which is simultaneously accumulating on its walls.

SUMMARY.

The ionization currents from clouds dispersed in air from a zinc arc and from the decomposition of zinc ethyl have been described. The cloud particles in both cases are crystalline, with the internal structure of zincite. The clouds from the arc are ionized on formation ; those from zinc ethyl are not.

There seems to be a spontaneous production of ions in these clouds as they age. In the case of clouds from zinc ethyl the ionization increases from zero to a maximum intensity and then diminishes. Qualitatively the intensity increases with the amount of material dispersed and with the degree of dispersion.

The initial ionization in clouds from the arc is attributed to thermoelectric emission of charges at the high temperature of formation. With a cloud of low concentration this diminishes with time and is the dominant effect. The coefficient of recombination of these ions is found to be of the same order of magnitude as the coagulation constant of similar clouds.

With increasing concentration of dispersion the two effects are superposed.

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LIX. *Forced Surface-Waves on Water.*

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1. THE following notes deal with some problems of forced waves on the surface of water, the waves being forced in that the normal fluid velocity has an assigned value at every point of a given vertical surface; the problems treated here are the elementary cases when the given surface is an infinite plane or a circular cylinder. The motion of the water surface consists in general of travelling waves together with a local disturbance, and the type of solution is one which may have possible application to the waves produced in water by the small oscillations of a solid body.

2. Consider first deep water, and take the origin in the free surface with Ox horizontally and Oz vertically downwards. The velocity potential satisfies

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} = 0. \quad (1)$$

Neglecting the square of the fluid velocity at the free surface, and omitting the effect of capillarity, the condition at the free surface is

$$\frac{\partial^2 \phi}{\partial t^2} - g \frac{\partial \phi}{\partial z} = 0, \quad (2)$$

and the surface elevation ζ is given by

$$\zeta = \frac{1}{g} \left(\frac{\partial \phi}{\partial t} \right)_{z=0} \quad (3)$$

For simple harmonic motion we assume a time-factor $e^{i\sigma t}$, and (2) gives

$$\kappa_0 \phi + \frac{\partial \phi}{\partial z} = 0, \text{ at } z=0, \quad (4)$$

with $\kappa_0 = \sigma^2/g$.

Suppose now that we are also given

$$-\frac{\partial \phi}{\partial x} = f(z) e^{i\sigma t}, \text{ at } x=0, \quad (5)$$

where $f(z)$ is given for all positive values of z ; and we require a solution of (1), (4) and (5) suitable for positive values of x .

* Communicated by the Author.

The solution can be obtained by various methods; for example, by combining suitable elementary solutions of (1) and (4). The usual solution for free progressive waves is found from

$$\phi = e^{-\kappa_0 z - i\kappa_0 x}. \quad \quad (6)$$

There is also another elementary solution,

$$\phi = e^{-\kappa x} (\kappa \cos \kappa z - \kappa_0 \sin \kappa z), \quad \quad (7)$$

where κ may have any real positive value.

We can generalize these solutions by means of the following integral theorem, which may easily be verified:

$$\begin{aligned} f(z) = & \frac{2}{\pi} \int_0^\infty \int_0^\infty f(\alpha) \frac{(\kappa \cos \kappa z - \kappa_0 \sin \kappa z)(\kappa \cos \kappa \alpha - \kappa_0 \sin \kappa \alpha)}{\kappa^2 + \kappa_0^2} d\kappa d\alpha \\ & + 2\kappa_0 e^{-\kappa_0 z} \int_0^\infty f(\alpha) e^{-\kappa_0 \alpha} d\alpha. \quad \end{aligned} \quad (8)$$

Here $f(z)$ is given for all positive values of z , and it should be remarked that the proof involves the Fourier integral theorem, and that $f(z)$ is subject to suitable limitations.

We may now write down a solution which satisfies the condition (5). It is clear that, on the forced vibrations so obtained, we may superpose any free oscillations for which $\partial\phi/\partial x$ is zero over the plane $x=0$; we shall choose the latter so that the complete solution represents waves travelling outwards for large positive values of x . This solution is given by

$$\begin{aligned} \phi = & 2e^{-\kappa_0 z} \sin(\sigma t - \kappa_0 x) \int_0^\infty f(\alpha) e^{-\kappa_0 \alpha} d\alpha + \frac{2}{\pi} \cos \sigma t \\ & \times \int_0^\infty \int_0^\infty f(\alpha) \frac{(\kappa \cos \kappa z - \kappa_0 \sin \kappa z)}{\kappa(\kappa^2 + \kappa_0^2)} e^{-\kappa x} d\kappa d\alpha. \quad . \end{aligned} \quad (9)$$

This gives a normal velocity $f(z) \cos \sigma t$ over the plane $x=0$, and reduces to a positive wave for large positive values of x . The corresponding surface elevation is

$$\begin{aligned} \xi = & \frac{2\sigma}{g} \cos(\sigma t - \kappa_0 x) \int_0^\infty f(\alpha) e^{-\kappa_0 \alpha} d\alpha \\ & - \frac{2\sigma}{\pi g} \sin \sigma t \int_0^\infty \int_0^\infty f(\alpha) \frac{\kappa \cos \kappa \alpha - \kappa_0 \sin \kappa \alpha}{\kappa^2 + \kappa_0^2} e^{-\kappa x} d\kappa d\alpha. \end{aligned} \quad (10)$$

The first term of (10) is a plane progressive wave of the

same wave-length as the free wave of the same frequency, while the second term may be called the local oscillation.

If we take $f(z) = e^{-\kappa_0 z}$, the second term in (9) and (10) vanishes, and we regain the expressions for a simple progressive wave.

If we take, more generally,

$$f(z) = Ae^{-pz} \dots \dots \quad (11)$$

over the whole range for z , the second integral in (10) can be evaluated explicitly in terms of Cosine and Sine integrals, and we obtain

$$\begin{aligned} \zeta = & \frac{2\sigma A}{\kappa_0 + p} \cos(\sigma t - \kappa_0 x) - \frac{2\sigma A \sin \sigma t}{\pi g(\kappa_0 + p)} \\ & \times [\text{Ci}(px) \cos px - \text{Ci}(\kappa_0 x) \cos \kappa_0 x + \text{Si}(px) \sin px \\ & - \text{Si}(\kappa_0 x) \sin \kappa_0 x - \frac{\pi}{2} (\sin px - \sin \kappa_0 x)]. \end{aligned} \quad (12)$$

As we make p smaller we approach the limiting case of constant normal velocity over the whole of the plane $x=0$. It is of interest to note that the amplitude of the travelling wave remains finite in the limit, but that the amplitude of the local oscillation becomes logarithmically infinite at $x=0$.

3. A problem of some interest is the decay of the vertical oscillations of a floating body due to the propagation of waves outwards from it, but a direct attack upon the problem is difficult. We may perhaps obtain a rough estimate by applying the preceding analysis to a simplified form of the problem. Imagine a log of rectangular section floating in water with the sides vertical; let b be the breadth and d the depth immersed. Now suppose the log made to execute small vertical oscillations of amplitude a and frequency σ . Let one of the sides of the log lie in the plane $x=0$; then the disturbance in the water on that side may be regarded as due to a certain oscillating distribution of normal fluid velocity over the plane $x=0$ from $z=d$ to $z=\infty$. If we make the assumption that this is of the form

$$f(z) \cos \sigma t, \dots \dots \quad (13)$$

then, from continuity of flow, we have

$$2 \int_d^{\infty} f(z) dz = \sigma ab. \dots \dots \quad (14)$$

Without attempting to solve the actual problem, let us assume

$$f(z) = Ae^{-pz}; \dots \dots \quad (15)$$

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then from (14) we have

$$A = \frac{1}{2} \sigma ab p e^{pd}. \quad \dots \quad (16)$$

From (10) we find that the amplitude of the waves travelling out on either side of the log would be

$$\begin{aligned} & \frac{\sigma^2 ab p}{g} e^{pd} \int_d^\infty e^{-(\kappa_0 + p)\alpha} d\alpha \\ &= \frac{\sigma^2 ab p}{g(\kappa_0 + p)} e^{\kappa_0 d}. \quad \dots \quad (17) \end{aligned}$$

A large value of p would correspond to a concentration of the outward flow round the lower edges of the log; hence this estimate gives, as an upper limit for the amplitude,

$$(\sigma^2 ab/g) e^{-\sigma d/g}. \quad \dots \quad (18)$$

4. If, in the general problem of §2, the normal velocity at $x=0$ is a function of y as well as of z , the solution of the three-dimensional motion can be obtained by an additional Fourier synthesis.

Assume first that ϕ is proportional to $\cos \kappa'(y - \beta)$, then the potential equation is

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} - \kappa'^2 \phi = 0. \quad \dots \quad (19)$$

The time entering as a simple harmonic factor, the boundary condition at $z=0$ is given by (4).

We have now the following elementary solutions, omitting the factors in y and t :

$$\begin{aligned} \phi &= e^{-\kappa_0 z - i\epsilon(\kappa_0^2 - \kappa'^2)^{\frac{1}{2}}}, \text{ for } \kappa' < \kappa_0; \\ \phi &= e^{-\kappa_0 z - i\epsilon(\kappa'^2 - \kappa_0^2)^{\frac{1}{2}}} \text{ for } \kappa' > \kappa_0; \\ \phi &= e^{-z(\kappa^2 + \kappa'^2)^{\frac{1}{2}}} (\kappa \cos \kappa z - \kappa_0 \sin \kappa z). \quad \dots \quad (20) \end{aligned}$$

The theorem (8) may be generalized, with suitable limitations on the function $f(y, z)$, to

$$\begin{aligned} f(y, z) &= \frac{2\kappa_0}{\pi} e^{-\kappa_0 z} \int_0^\infty d\alpha \int_{-\infty}^\infty d\beta \int_0^\infty f(\alpha, \beta) e^{-\kappa_0 \alpha} \cos \kappa'(y - \beta) d\kappa' \\ &+ \frac{2}{\pi^2} \int_0^\infty d\alpha \int_0^\infty d\kappa \int_{-\infty}^\infty d\beta \int_0^\infty f(\alpha, \beta) \\ &\quad (\kappa \cos \kappa z - \kappa_0 \sin \kappa z) \\ &\quad \times \frac{(\kappa \cos \kappa \alpha - \kappa_0 \sin \kappa \alpha)}{\kappa^2 + \kappa_0^2} \cos \kappa'(y - \beta) d\kappa' \quad (21) \end{aligned}$$

Suppose that at $x=0$ we are given

$$-\frac{\partial \phi}{\partial x} = f(y, z) \cos \sigma t. \quad \dots \quad (22)$$

Then from (20) and (21) we obtain an expression for ϕ , valid for positive values of x , and adjusted so that it represents progressive waves at large values of x ; we find

$$\begin{aligned} \phi = & \frac{2\kappa_0}{\pi} e^{-\kappa_0 z} \int_0^\infty d\alpha \int_{-\infty}^\infty d\beta \int_0^{\kappa_0} j'(\alpha, \beta) \sin (\sigma t - x \sqrt{\kappa_0^2 - \kappa'^2}) \\ & \times \frac{e^{-\kappa_0 x} \cos \kappa'(y - \beta)}{(\kappa_0^2 - \kappa'^2)^{\frac{1}{2}}} d\kappa' + \frac{2\kappa_0}{\pi} e^{-\kappa_0 z} \cos \sigma t \int_0^\infty d\alpha \int_{-\infty}^\infty d\beta \int_{\kappa_0}^\infty \\ & \times f'(\alpha, \beta) e^{-x(\kappa'^2 - \kappa_0^2)^{\frac{1}{2}} - \kappa_0 \alpha} \cos \kappa'(y - \beta) d\kappa' + \frac{2}{\pi^2} \cos \sigma t \\ & \times \int_0^\infty d\alpha \int_0^\infty d\kappa \int_{-\infty}^\infty d\beta \int_0^\infty f(\alpha, \beta) e^{-x(\kappa^2 + \kappa'^2)^{\frac{1}{2}}} \cos \kappa'(y - \beta) \\ & \times \frac{(\kappa \cos \kappa z - \kappa_0 \sin \kappa z)(\kappa \cos \kappa \alpha - \kappa_0 \sin \kappa \alpha)}{(\kappa^2 + \kappa_0^2)(\kappa^2 + \kappa'^2)^{\frac{1}{2}}} d\kappa'. \quad \dots \quad (23) \end{aligned}$$

A particular case which would illustrate the spreading of plane waves emerging from a canal into an infinite sea is obtained by taking

$$f(y, z) = (ga\kappa_0/\sigma) e^{-\kappa_0 z} \cos \sigma t, \quad \dots \quad (24)$$

over the whole range for z and between the limits $\pm b$ for y , the function being zero outside these limits for y . Substituting in (23), the third term disappears, and also the integrations with respect to β can be effected in the remaining terms. We find that the surface elevation for this case is given by

$$\begin{aligned} \xi = & \frac{2\kappa_0 a}{\pi} \int_0^{\kappa_0} \frac{\sin \kappa' b \cos \kappa' y \cos \{\sigma t - x(\kappa_0^2 - \kappa'^2)^{\frac{1}{2}}\}}{\kappa'(\kappa_0^2 - \kappa'^2)^{\frac{1}{2}}} d\kappa' \\ & - \frac{2\kappa_0 a}{\pi} \cos \sigma t \int_{\kappa_0}^\infty \frac{\sin \kappa' b \cos \kappa' y e^{-x(\kappa'^2 - \kappa_0^2)^{\frac{1}{2}}}}{\kappa'(\kappa'^2 - \kappa_0^2)^{\frac{1}{2}}} d\kappa'. \quad \dots \quad (24) \end{aligned}$$

The form of the surface could be studied by approximate evaluation of these integrals as in similar diffraction problems.

5. We return to plane waves, and suppose now that the water is of finite depth h . We have the additional condition

$$\frac{\partial \phi}{\partial z} = 0, \text{ for } z=h. \quad \dots \quad (25)$$

The corresponding elementary solutions are

$$\phi = e^{i(\sigma t - \kappa_0 x)} \cosh \kappa_0(z-h), \dots \quad (26)$$

where κ_0 is the real positive root of

$$g\kappa_0 \tanh \kappa_0 h = \sigma^2; \dots \quad (27)$$

and

$$\phi = e^{i\sigma t - \kappa x} \cos \kappa(z-h), \dots \quad (28)$$

where κ is any real positive root of

$$g\kappa \tan \kappa h + \sigma^2 = 0. \dots \quad (29)$$

This equation has an infinite sequence of real roots, together with an imaginary root $i\kappa_0$. We assume then the possibility of expanding a function $f(z)$ in the range $0 \leq z \leq h$, in the form

$$f(z) = A \cosh \kappa_0(z-h) + \sum B \cos \kappa(z-h), \dots \quad (30)$$

where the summation extends over the real positive roots of the equation (29). We find that the coefficients are given by

$$A = \frac{4\kappa_0}{2\kappa_0 h + \sinh 2\kappa_0 h} \int_0^h f(\alpha) \cosh \kappa_0(\alpha-h) d\alpha,$$

$$B = \frac{4\kappa}{2\kappa h + \sin 2\kappa h} \int_0^h f'(\alpha) \cos \kappa(\alpha-h) d\alpha. \dots \quad (31)$$

If at $x=0$ we are given

$$-\frac{\partial \phi}{\partial x} = f(z) \cos \sigma t, \dots \quad (32)$$

then the velocity potential for positive values of x , such that the motion at a distance is a plane progressive wave, is given by

$$\phi = A \kappa_0^{-1} \cosh \kappa_0(z-h) \sin (\sigma t - \kappa_0 x) + \sum B \kappa^{-1} e^{-\kappa x} \cos \kappa(z-h) \cos \sigma t. \dots \quad (33)$$

Suppose, for instance, that one end of a long tank is made to execute simple harmonic vibrations of small amplitude a , then we have $f(z) = \sigma a$. The values of A and B follow from (31), and from (33) we deduce the surface elevation in this case :

$$\zeta = \frac{2\sigma^2 a \sinh 2\kappa_0 h}{g\kappa_0(2\kappa_0 h + \sinh 2\kappa_0 h)} \cos(\sigma t - \kappa_0 x) - \sin \sigma t \sum \frac{2\sigma^2 a e^{-\kappa x} \sin 2\kappa h}{g\kappa(2\kappa h + \sin 2\kappa h)}. \dots \quad (34)$$

6. The same analysis may be applied to circular waves, and we limit consideration here to symmetry round the origin. The normal fluid velocity is supposed to be assigned over a vertical cylindrical surface; for example, we take

$$-\frac{\partial \phi}{\partial r} = f(z) \cos \sigma t, \text{ for } r=a. \quad \dots \quad (35)$$

The velocity potential satisfies

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{\partial^2 \phi}{\partial z^2} = 0. \quad \dots \quad (36)$$

The condition at the free surface is the same as before, and we assume the water to be deep. Elementary solutions of the required form are found in terms of suitable Bessel functions. The solution

$$\phi = e^{i\sigma t - \kappa_0 z} H_0^{(2)}(\kappa_0 r) \quad \dots \quad (37)$$

represents diverging waves for large values of r ; while in the solution

$$\phi = e^{i\sigma t} (\kappa \cos \kappa z - \kappa_0 \sin \kappa z) K_0(\kappa r), \quad \dots \quad (38)$$

$K_0(\kappa r)$ tends exponentially to zero for large distances from the origin.

Generalizing as before, we obtain the solution

$$\begin{aligned} \phi = & 2e^{i\sigma t - \kappa_0 z} \frac{H_0^{(2)}(\kappa_0 r)}{H_1^{(2)}(\kappa_0 a)} \int_0^\infty f(\alpha) e^{-\kappa_0 \alpha} d\alpha - \frac{2}{\pi} e^{i\sigma t} \\ & \times \int_0^\infty \left\{ \int_0^\infty f(\alpha) \frac{K_0(\kappa r)}{\kappa K_0'(\kappa \alpha)} \frac{(\kappa \cos \kappa z - \kappa_0 \sin \kappa z)}{(\kappa \cos \kappa \alpha - \kappa_0 \sin \kappa \alpha)} d\kappa d\alpha \right\}, \quad (39) \end{aligned}$$

where the real part is to be taken.

The surface elevation at a great distance from the origin is given by

$$\xi \sim -\frac{2i\sigma}{g} \left(\frac{2}{\pi \kappa_0 r} \right)^{\frac{1}{2}} J_0'(\kappa_0 a) - i Y_0'(\kappa_0 a) \int_0^\infty f(\alpha) e^{-\kappa_0 \alpha} d\alpha, \quad (40)$$

or, in real terms, this gives

$$\begin{aligned} \xi \sim & -\frac{2\sigma}{g} \left(\frac{2}{\pi \kappa_0 r} \right)^{\frac{1}{2}} \int_0^\infty f(z) e^{-\kappa_0 \alpha} d\alpha \\ & \times \frac{J_0'(\kappa_0 a) \sin(\sigma t - \kappa_0 r + \frac{1}{4}\pi) + Y_0'(\kappa_0 a) \cos(\sigma t - \kappa_0 r + \frac{1}{4}\pi)}{J_0'^2(\kappa_0 a) + Y_0'^2(\kappa_0 a)}. \quad \dots \quad (41) \end{aligned}$$

This expression might be used, as in §3, to give an estimate for the energy propagated outwards from a circular cylinder immersed to a given depth, and making small vertical oscillations of given frequency.

LX. *The Work of Sir Joseph Larmor**.
By Sir OLIVER LODGE.

I DO not envy the historian who shall some day attempt to write the history of the development of modern physics, and shall attempt to assign due credit to the 19th century mathematicians for their contribution to whatever it is that shall survive out of the present 20th century turmoil. That great and surprising progress is being made is fairly evident, but what may be its quasi permanent form when the revolution has ended, and things have settled down again, who can say? The younger generation of mathematical physicists, absorbed in their brilliant abstractions, and vying with each other in the best mode of expressing them—sometimes without even attempting to form clear physical conceptions of the underlying realities which their equations must be supposed to represent—are apt to ignore the work of their predecessors, and to regard the old-fashioned methods as antiquated and superseded.

The historian, however, will, I anticipate, not take that view. He will, I hope, realise that the whole advance is a consistent evolution, and will be able to detect in the work of the leaders of the 19th century the germ of many ideas which by his time will have blossomed and borne fruit. To undertake such an historical survey at the present time would be hopelessly impossible, even for the best informed. Many theories are struggling for existence, and no one can tell in what form the fittest will survive. But one can safely say that whoever hereafter undertakes the work will find in these volumes of the Collected Papers of

* 'Mathematical and Physical Papers,' by Sir Joseph Larmor. In two volumes. £6 6s. net. Vol. i. pp. 679+xii; vol. ii. pp. 831+xxxii., with Prefaces, Notes, Index, and Appendices. (Cambridge University Press.)

Sir Joseph Larmor, a great mass of material, some of which must be discarded, but nearly all of which will be recognised as steps in the ladder of progress. And it is not unlikely that some of the ideas which now seem to be superseded by the modern points of view may revive and take their place in the ultimate coherent scheme, when the abstractions have once more become concrete, and when return to physical conceptions is possible.

Consequently, I think that Sir Joseph Larmor has performed a great service, not only in collecting his Papers into readily accessible form, but in editing them and as far as possible bringing them up to date by new footnotes and appendices and elucidatory remarks. He, himself, has done good work, as an incipient historian of the 19th century, by his Obituary Notices of some of the workers, and especially by his critical appreciation of the work of Lord Kelvin during those fruitful years of the 1840's before he was partially diverted from pure science by cable and other engineering developments, and while he was laying the foundation of thermodynamics and many another important subject, doing work which at that time no one else was competent to do. It seems a pity that these careful studies of early work should be excluded from the present volumes by pressure of other matter, and I venture to hope that the Cambridge University Press may contemplate the production of yet a third or supplementary volume, thinner than the other two, which shall include and make easily accessible all the present omissions, some of which are referred to in the Preface to vol. ii. For when we have been favoured with the life-work of a man of exceptional power and industry, it behoves us to make what use we can of it, and to make it available for the study of posterity, who by that time will doubtless have a criterion of value more serviceable than any we possess at present, and will not only find it of interest to recognise the intuitions of the great men of the past, but will be helped in their formulation of truth by the continuous thread of thought which runs through the labyrinth, and leads towards the ultimate, though even then still unreached, goal.

The time is as yet far distant for such a task to be undertaken even by a learned and leisurely historian. Anyone who has been trained in the methods of the 19th century must be liable to gasp when extracted from his habitual

medium into the rarefied atmosphere of the 20th century. Some will undoubtedly shine with undiminished lustre ; such an one as Clerk Maxwell, for instance. The clarifying work of the late Lord Rayleigh cannot but be always useful. But what the verdict of history will be on the later work of Lord Kelvin, the less voluminous but brilliant intuitions of G. F. Fitzgerald, the steady contributions of Poynting, and the contemporary work of Sir J. J. Thomson and Sir Joseph Larmor I do not presume to judge ; though I may be permitted to guess that some of this work will be valued more highly than it is at present, and in the light of clearer knowledge will be better understood.

We, of this and future generations, surely ought to feel grateful for the strenuous labours of a mathematician who, living a secluded life in his rooms at St. John's College, Cambridge, has devotedly concentrated on problems of exceeding difficulty. Having put aside nearly all other interests, he must have laboured, ever since his Senior Wranglership, to absorb all the learning of his time in this department of knowledge, to subject it to critical examination, and to develop it further for his own satisfaction and for the benefit of his co-workers. Incidentally, he must have thus saved some pioneering work from destruction. Clerk Maxwell's and Rayleigh's, and I suppose Lorentz's, might be trusted to survive anyhow ; but without Larmor I venture to think that Lord Kelvin's theoretical seeds might gradually sink into oblivion. Not in their original form will they continue to bear fruit ; but the output of so great a genius, in spite of occasional narrownesses and mistakes, ought to exert a permanent and abiding influence, now that the clouds of which he complained are partially cleared away, and when the nature of fundamental reality is perhaps becoming better understood.

The Collected Papers of the great mathematical physicists are exceedingly useful to present and future students, and are of especial value when the author himself takes the trouble to collect and edit them with footnotes and appendices. The Collected Papers of Stokes, Kelvin, and Rayleigh constitute a monument of the end of the 19th century, as Thomas Young's Papers were for the beginning. And now Larmor's Papers link the two centuries together.

From another point of view these two volumes may be said to constitute the high-water mark of mathematical physics prior to the dawn of the 20th century.

To review these majestic volumes adequately is for any single writer impossible, even if he were qualified to understand the whole of their contents, which in the present instance is far from being the case. I can only pick out a few salient features on a few points of interest, and express admiration for the genius and learning displayed by them.

The whole question of rotational elasticity in space is not one to be lightly dealt with or criticised. I venture to think that more will be heard of it hereafter, and that Larmor is one of the pioneers. Absolute rotation is insisted on; and with regard to Newtonian absolute space and time. Larmor perceives that some of the philosophic or metaphysical complications introduced by Relativity are due to our practical dealing with space and time by means of light signalling. If light had happened to travel instantaneously, those difficulties would not have arisen. And even now absolute space and time are coherent as a logical scheme, because we can *imagine* instantaneous signalling: it is only impracticable when we have to depend on light. I have myself argued in the same direction, that we can *think* of simultaneity at a distance, though we cannot perceive it by any laboratory methods, and that accordingly undue philosophic emphasis ought not to be laid on considerations only made valid or plausible by the finite velocity of light.

On page 411 of vol. ii. there are some observations on the anthropomorphic nature of the dissipation of energy as expressed by Kelvin, and on Kelvin's treatment of the energy available to man for mechanical effect; an anthropomorphism which survived in modified form in Maxwell's demons.

A paper which really settled the question of why wireless waves can bend round the earth, a theory only partially anticipated by Dr. Eccles, will be found as Article 100.

Concerning metallic conduction, reasons are given for the number of electrons taking part in conveying a current. The argument makes the number of virtually free electrons in a molecule comparable with the number of

molecules, so that the mean free path is exceedingly short, and the velocity comparatively low.

There are some remarkable Appendices to vol. ii. beginning with Abstracts from Reports of the British Association, continuing with statistical methods in thermodynamics and limitations of equipartition, molecular scattering of radiation, time and space of astronomical observers, and concluding with such notable titles as "Mind, Nature and Atomism," and "Synoptic View of a Physical Universe as Optically Apprehended." There are also Appendices to vol. i. on Radiation from Accelerated Electrons, on Maxwell's Stress and Radiation Pressure, on the Repulsion of Bodies by Radiation, on the Inertia of Aggregation, and on Gyromagnetics.

I merely summarise these things briefly to show that in these volumes, in addition to mathematical analysis, there is a good deal that any educated reader might find of interest, some of it clearly, and all of it powerfully, presented.

On the whole I think the future historian will be most interested and most impressed by the content of vol. i., which carries the Papers up to the end of the 19th century. The beginnings of the electrical theory of matter and a theory of electrons are to be found in that comprehensive and masterly Phil. Trans. Memoir, dated 1894 and 1895, called "A Dynamical Theory of the Electric and Luminiferous Medium," covering over 200 pages in vol. i. and carried forward, in its application to material media, into vol. ii. where after another 100 pages it blends into the dynamics of a system of electrons or ions and the optical influence of a magnetic field. An attempt is here made at a rotational elastic fluid ether, and though such a medium has temporarily gone out of fashion, I fully expect its revival in some still more developed form hereafter. The famous Lorentz transformation to moving axes, called for by the nul result of the M.M. experiment made by moving observers, and utilised as an expression of the earliest Relativity theory, is here begun, and it is remarkable how much detailed knowledge about electrons is shown before the final discovery of those bodies.

There are some interesting remarks on the Poincaré pressure and its application to electron theory. Indeed, the whole treatment of electron theory will need careful

attention by the historian of the future. The author's dissatisfaction with the concealment or sophistication of the positive electron is manifest, and several times we find him exclaiming, in one form or another, "The problem of the positive electron remains."

The extremely general analysis introduced by Lagrange is the inevitable method of dealing with a medium whose physical properties and mechanism are absolutely unknown. Whether any real progress has been made towards an explanation of the universe in terms of a rotational fluid is a question that can only be answered by posterity. To me this idea seems more and more hopeful as time goes on, and it seems likely to be the ultimate elucidation of wave dynamics. At present this is little more than a pious opinion, and much further work is necessary before it can be consolidated into a comprehensive theory of physical existence. If ever it becomes possible to regard it in a still more inclusive manner as affording a physical basis for vital and mental phenomena, then philosophers of the future will owe a debt of gratitude to the pioneers who have groped their way through the present tangle into a brighter and more luminous region beyond.

The brief notes or summaries of the argument, which the author has been permitted by the Cambridge University Press to put in the margin of the pages, are a great help, not only to anyone looking through the book, but even as an elucidation of the text.

The author has prepared a comprehensive index to each of the volumes, but unfortunately both Indexes are printed at the end of the second volume. In a future edition this might be remedied, so that each volume might be self-contained.

But it may be said, Are there no other faults to be found with the production? Is there nothing that could have been put better? That I by no means claim. I find certain defects of style, which militate against a clear apprehension, or at any rate any rapid apprehension, of the meaning of the author. It is an unkindly act to criticise style, for style they say is the man. The author might well claim that his vagueness, whenever vagueness has to be admitted, is no more than is inevitable, and that attempted over-clearness would suggest a definiteness of knowledge which does not exist. He might also claim that

the involved parentheses, which sometimes spoil the run of his sentences, do not really confuse the meaning, but are necessary to its guarded presentation, and in this he could doubtless claim the example of Lord Kelvin. Still, I do venture to say that, apart from the mathematics, the style might be simpler. I sometimes think that even the mathematical expressions are not set forth with that clearness and efficiency which may be said to characterise the memoirs of H. A. Lorentz, for instance, and other Continental physicists : so that sometimes it unfortunately happens that fruitful expressions and valuable points of view are attributed to one or other of these writers, rather than to Larmor who was the first to state them, in rather a concealed and unemphasised manner. It may be the Cambridge method to write down results without emphasis, and without trying to elaborate their full meaning, trusting to disciples to do this spade work. Sometimes those disciples are forthcoming, but sometimes they are not, and so the work of the master gets overlooked, until rediscovered independently by others.

It may perhaps be said that I ought not to accuse my friend of an involved style without giving some example. Well, it is an ungrateful task, but here is an unfavourably chosen sentence taken from page xii. of vol. ii. He is referring to the problem of modes of vibration of a set of atomic singularities embedded in an isotropic elastic medium with certain properties, and seeking to assimilate the early methods of Stokes and Lamé with the recent equations of Schrödinger. But I find it difficult to understand what is meant by the following sentence :—

“ For, pursuing the analogy, if the electric singular points of the æthereal vibrating system of the atom are not to be also singularities after the manner of the actual vesicles filled with compressed gas that occur in crystals, from or to which intense hydrostatic pressure radiates other than the intrinsic electrically sustained constant universal pressure aforesaid—and any such added source of pressure would probably spoil the type of model of a convected electron—we are invited to seek out forms of solution for disturbance superposed on this intrinsic æthereal pressure, adapted to the local field of the atom, of types which indeed converge radially on the positions of its electrons or other nuclei in a way prescribed by their electric field, but without tendency towards values there

increasing without limit ; for stable modes of local vibration of the ambient æther could only occur around the definite configurations of the material atom permitting of such solutions of the pressure-equation. which alone could subsist."

There may be a lot of meaning in this, but it is not easy to disentangle.

Least Action methods are, of course, constantly employed, even in one of the earlier Papers dated 1884, and later on, in this same method, the beginnings of Schrödinger's wave theory can be traced. It may possibly come as a surprise to 20th century physicists, if they allow themselves to read these volumes, how much anticipation there is in these great 19th century Memoirs.

A treatment of the action of magnetism on light, and a correlation of optical theories, many of which though now discarded are full of interest, constitute Memoir 34 of vol. i. and of date 1893. The outstanding difficulty about radiation from a radially accelerated electron is discussed in an Appendix, page 650.

It is hopeless to go into details. I can only draw attention to a few salient features, of which others will find many more instances, some of fundamental and some of historical importance.

For instance, the mathematics of group waves and their treatment by Fourier's methods are usefully dealt with in a Paper on Harmonic Analysis dated 1916. Article 90. And it is noteworthy that even at that date there is an italic heading that energies of groups must be regarded atomically, and again that the energy of a group must be treated as an indivisible whole. He appears to say that travelling energy must come in atomically by group aggregates alone, like the energy of a vortex ring in hydro-dynamics or of a travelling electron. He recognzies that such groups are disentangled by dispersion, and that there can be an abrupt pulse in a dispersive medium, such as is suggested by the recent work of G. P. Thomson and others.

There is a good deal of discussion on group waves and their atomic character, and Fourier analysis is applied to sum up a large number of component waves. For the atomic energy of groups, page 551 may be referred to.

In an Address given to Section A at the Bradford Meeting of the British Association in 1900 the author, among other things, discusses the relative advantage of physical models

and mathematical abstractions (see page 213 of vol. ii.). He says :—

“ The abstract standpoint is always attained through the concrete : and for purposes of instruction such models, properly guarded, do not perhaps ever lose their value : they are just as legitimate aids as geometrical diagrams, and they have the same kind of limitations.”

“ Gradual transition into abstract statement of physical relations amounts to retaining the essentials of our working models while eliminating the accidental elements involved in them . . . We cannot expect to mentally grasp all aspects of the content of even the simplest phenomena . . . In Maxwell’s words. ‘ For the sake of persons of different types, scientific truth should be presented in different forms, and should be regarded as equally scientific whether it appear in the robust form and vivid colouring of a physical illustration, or in the tenuity and paleness of a symbolical expression.’ ”

And as illustrating the kind of desperation which seizes some investigators at the multiplicity and complexity and unsatisfactory character of present-day theories, the despairing opinion of Thomas Young is quoted, at the date 1817 when his faith in the undulatory theory of light had been eclipsed by Malus’ discovery of polarisation by reflection, before the mystery had been solved (in so far as it was solved) by Fresnel. This difficulty, he says, “ will probably long remain, to mortify the vanity of an ambitious philosophy, completely unresolved by any theory.”

A feeling akin to despair must occasionally arise in the minds of all but the youngest when confronted with the amazing amount of still unresolved ignorance about existence in general, and it is comforting that even so great a man as Thomas Young could share that feeling.

These volumes constitute an amazing mass of information in almost every department of physics. They are a tribute to the insight and analytic power of the author, and they will probably long be referred to by investigators who are reaching what after all may be somewhat similar conclusions by other methods, and in a form susceptible of clearer and completer statement, by reason of the additional knowledge still constantly accruing.

LXI. *Precision Measurements of X-Ray Reflexions
from Crystal Powders.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

THE recent paper by J. Brentano and J. Adamson⁽¹⁾ on "Precision Measurements of X-ray Reflexions from Crystal Powders" has attracted my attention. These authors give the lattice parameter of cadmium oxide as $4\cdot683 \pm \cdot004$ A. Pierre van Dyck, formerly of this laboratory, made precision measurements on cadmium oxide using the powder method and the standard X-ray diffraction apparatus by Davey⁽²⁾ and manufactured by the General Electric Company. The value obtained was $4\cdot681 \pm \cdot002$ A. This letter is written as an excellent check on the work of Brentano and Adamson and as an illustration of the comparative accuracies of the focusing method of Brentano⁽³⁾, and the simpler but equally precise method of Davey⁽⁴⁾. The lack of agreement between the values obtained by Brentano and Adamson and by van Dyck, and those obtained by Davey and Hoffman⁽⁵⁾, P. Scherrer⁽⁶⁾, and H. P. Walmsley⁽⁷⁾, which vary from 4·699 to 4·72, is probably due to differences in the purity of the specimens used.

P. van Dyck obtained the value 4·681 with a very pure sample of cadmium oxide which has been made by burning in air vacuum distilled cadmium metal, which was shown by spectrographic analysis to contain only very faint traces of zinc and lead. A pure grade of commercial cadmium oxide, which contained small amounts of carbon dioxide, zinc oxide and other foreign matter, was also measured. The value obtained was the same as that obtained with the extremely pure cadmium oxide. Cadmium oxide gives a powder pattern with unusually sharp diffraction maxima which lend themselves readily to precise measurement. This laboratory has often thought of using cadmium oxide as a reference standard for precision measurements by the powder method rather than sodium chloride. The diffraction maxima of cadmium oxide are much sharper than those of sodium chloride, and for the same exposure time a much wider range of accurately measurable lines is obtained.

The observed interplanar spacings for cadmium oxide, which were used in the calculations, are given below:—

Planar Indices.	Spacings.
110(2)	1·657
111(2)	1·351
100(4)	1·172
331	1·073
210(2)	1·046
511	0·901
111(3) }	
110(4)	0·828

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The New Jersey Zinc Coy.,
Pa., U.S.A.
July 1929.

Yours faithfully,
M. LUTHER FULLER,
Research Division.

LXII. Notices respecting New Books.

Astronomy and Cosmogony. Second edition. By Sir J. H. JEANS, F.R.S. (Cambridge University Press, Fetter Lane, London. Price 31s. 6d. net.)

THE first edition of this work appeared nine years after the author's 'Problems of Cosmogony and Stellar Dynamics,' and now the second edition has been called for within twelve months of the publication of the first, testimony that 'Astronomy and Cosmogony' has made a wide appeal not only to mathematicians and astronomers, but to the increasing number of educated laymen interested in modern scientific developments. The author's outstanding researches naturally play an important part in his review of the hypotheses put forward from the time of the earlier workers to the present day. The few pages of additional matter describe results obtained since the publication of the first edition, and in no way modify the general position taken up by Sir J. H. Jeans. A definite scheme of cosmogony is brought forward, but no claim is made that this is either complete

or even free from serious difficulties : the theories are set out "not in the belief that they will all prove to be true, but in the hope that the suggestions may in some degree help others ultimately to find the truth."

Introduction to Modern Physics. By F. K. RICHTMYER. (McGraw-Hill Publishing Co. Ltd., 6 & 8 Bouverie Street, London, E.C.4. Price 25s. net.)

PROF. RICHTMYER's book is largely based on courses of lectures given by him at Cornell University on the origin and development of the more important physical concepts, and is intended to prepare the way for the effective study of the new physics. From his wide experience as a teacher, the author has written a clear and admirable account of some of the modern physical theories, including the quantum theory of specific heats, the structure of the atom and the origin of spectra, X-rays, and the Compton effect. The first three chapters are devoted to a brief historical survey of the subject from the time of the Greeks to that of Faraday and Maxwell. Although Prof. Richtmyer disclaims any intention of bringing his lectures strictly up to date, he has introduced a number of topics which have been the subject of recent research. Bibliographies have not been appended to the chapters, but references are given in the text to original papers for the latest investigations. An extensive index of authors and subjects is provided, and appendices give the data of atomic structure and important physical constants. In binding and printing this volume reaches a high standard, and from its able presentation of modern physical developments can be recommended as a helpful introduction to the study of present-day physics.

The Viscosity of Liquids. By EMIL HATSCHEK. (Geo. Bell & Sons, Ltd., York House, Portugal Street, London, W.C.2. Price 15s. net.)

'Viscosity of Liquids' is a welcome addition to the International Text-books of Exact Science. From the very extensive literature contributed to scientific journals the author has selected for inclusion in his book many important experimental researches, especially those on the viscosity of solutions of electrolytes, liquid mixtures, and colloidal solutions. The interesting historical chapter is followed by the elementary mathematical theory of flow in a capillary tube and the annulus of two vertical coaxial cylinders, and the description of various types of viscometers, their design and use. Recent work on the variation of viscosity with temperature and with pressure is set out in the form of graphs and tables of experimental results, whilst copious references to original papers are given at the end of the chapters.

The Principles of Mechanics. By H. C. PLUMMER, F.R.S. (Geo. Bell & Sons, Ltd., York House, Portugal Street, London, W.C.2. Price 15s. net.)

THIS is an introductory course intended to prepare the reader for the further study of the advanced stages of the subject. The scope of the book may be indicated by noting that sections are devoted to the motion of a point in a plane, dynamics of translation, statics, including centres of gravity and friction, dynamics of a rigid body in two dimensions and in problems of elasticity, the torsion of cylinders, and the bending of rods. The notation of the differential and integral calculus is introduced and applied to the limited range of problems under discussion. Although the subject of the book is "Mechanics," not "Arithmetic," carefully chosen examples are given at the end of each chapter, with answers to the numerical exercises. A larger number of worked problems would have added to the value of the book and given the student experience in the application of principles and methods.

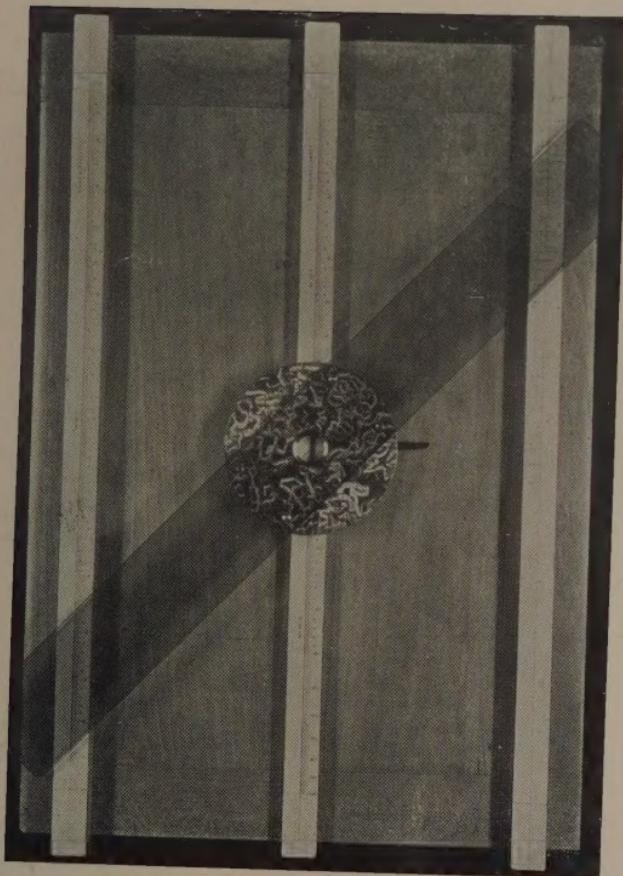
Polar Molecules. By P. DEBYE, Ph.D. (The Chemical Catalogue Co., 419 Fourth Avenue, at 29th Street, New York. Price \$3.50.)

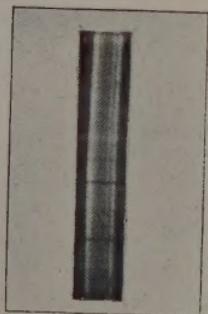
SOME seventeen years ago, Prof. Debye, from the study of the temperature variation of the dielectric constant, introduced the idea of molecular dipoles; he has now collected in this comprehensive volume the results of the numerous researches carried out during those years, and which have appeared largely in German scientific periodicals. Some experimental results are given here for the first time, and in all cases the author has been careful to give appropriate references. The author also makes suggestions for further experimental research in anomalous dispersion and electric saturation effects. In the study of the rotating diatomic molecule attention is drawn to the agreement between experiment and theory, that a molecular ray is partly attracted and partly repelled in a non-homogeneous electric field, the electric analogue of the Gerlach-Stern experiment. Prof. Debye has rendered good service in writing this monograph on the molecular interpretation of the dielectric constant, and in bringing together the widely-scattered contributions to recent theoretical and experimental research.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

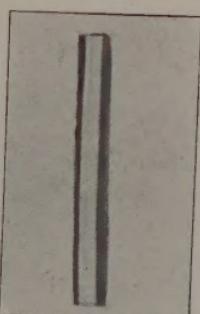
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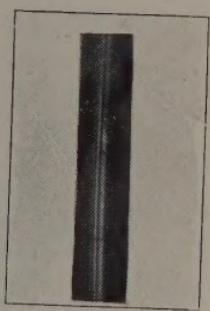
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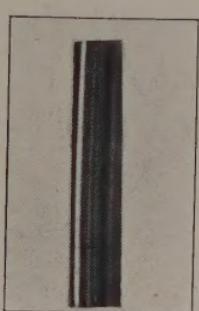
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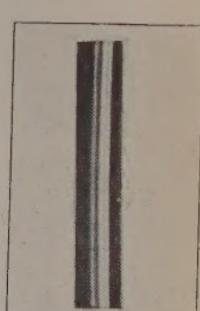
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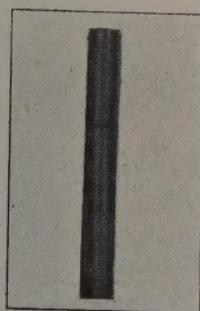
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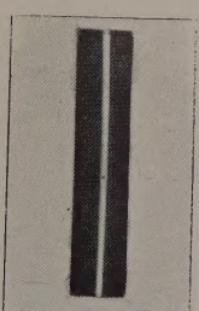
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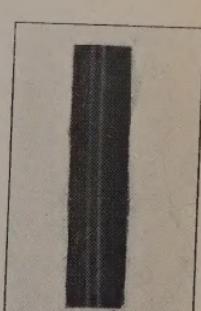
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